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Semi-annual summary research report in chemistry

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Semi-annual summary research report in chemistry

Abstract

A semi-annual summary research report in chemistry for the time period of July through December of 1955.

Keywords

Ames Laboratory

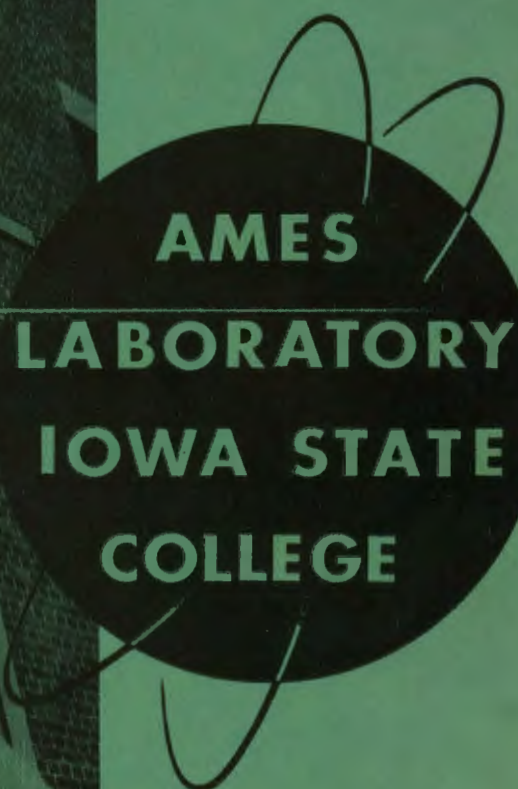
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ISC-706

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A.E.C. RESEARCH AND DEVELOPMENT REPORT

ISC-706



Physical Sciences Reading Room

CHEMISTRY. SEMI-ANNUAL SUMMARY RESEARCH REPORT

JULY-DECEMBER, 1955

UNCLASSIFIED

U N C L A S S I F I E D

ISC-706

U N I T E D S T A T E S A T O M I C E N E R G Y C O M M I S S I O N

SEMI-ANNUAL SUMMARY RESEARCH REPORT IN CHEMISTRY

For July - December, 1955

by

Ames Laboratory Staff

March 9, 1956

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Contract W-7405 eng-82

U N C L A S S I F I E D

U N C L A S S I F I E D

ISC-706

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U N C L A S S I F I E D

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Semi-Annual Summary Research Report in Chemistry

For the period July - December, 1955

This report is prepared from material
submitted by the group leaders of
the Laboratory

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Under the direction of F. H. Spedding, C. A. Goetz, C. V. Banks,
J. Corbett, A. H. Daane, F. R. Duke, V. A. Fassel, J. S.
Fritz, R. S. Hansen, G. Hammond, L. D. Jennings, D. S.
Martin, J. Powell, K. Ruedenberg, R. E. Rundle,
H. J. Svec and A. F. Voigt

Physical and Inorganic Chemistry

1. The Separation of Rare Earths by Ion-Exchange (F. H. Spedding and J. E. Powell)*

1.1 Pilot Plant Production of Pure Rare Earths and Yttrium

During the period of this report the pilot plant was used primarily for the production of pure "low cross-section" Y_2O_3 by the EDTA elution method, using cupric ion as the retaining ion.

In addition to high purity fractions of Y_2O_3 and Er_2O_3 , 19 kilograms of highly enriched fractions of Lu_2O_3 , Yb_2O_3 , Tm_2O_3 , Er_2O_3 , Ho_2O_3 and Dy_2O_3 and highly enriched fractions of Tb_4O_7 , Gd_2O_3 , Eu_2O_3 , Sm_2O_3 , Nd_2O_3 and Pr_6O_{11} were also obtained as a by-product of this work. Fractions having similar composition were combined and it is planned to complete the separation of these other rare earths in the near future.

A paper entitled "Basic Principles Involved in the Separation of Rare Earths by Ion Exchange" by F. H. Spedding and J. E. Powell was submitted for publication in J. Am. Chem. Soc.

Abstract

The separation of rare earth mixtures by ion exchange using ammonium ethylenediaminetetraacetate as an eluting agent and cupric ion as a retaining cation has been discussed in detail. Simple counter-current separation theory has been used to predict the minimum number of displacements of an adsorbed band that are necessary in order to separate the components of a binary mixture. It has been shown how the theory can be applied to even more complex systems and experimental data have been presented for some of the more difficultly separable groups of rare-earth species. Experimental results agree very well with the theoretical predictions.

*Names indicate group leaders in charge of work.

1.2 Exploratory Work in the Separation of Rare Earths by Ion Exchange

Preliminary investigations of diethylenetriaminepentaacetate solutions for the elution of rare earths are in progress. One interesting feature has been the shift of yttrium from the position between terbium and dysprosium observed with ethylenediaminetetraacetate and citrate elutions, to a position between neodymium and samarium in the case of diethylenetriaminepentaacetate elution. This effect may be of importance since this is the position where promethium should appear if it occurred naturally. Although promethium apparently does not occur naturally, it is noted that samarium and neodymium separate from each other more readily using either citrate or EDTA than do other neighboring rare earth pairs, because samarium and neodymium are not really adjacent rare earths. Therefore, it might be expected that separation factors for samarium and yttrium and for neodymium and yttrium with diethylenetriaminepentaacetate might be larger than the separation factors for terbium and yttrium, and dysprosium and yttrium with ethylenediaminetetraacetate or citrate. In other words, all other things being equal, it would be better to have yttrium fall in a position where an element was naturally missing than between two adjacent members of the series.

Work is progressing in an attempt to explain the mechanism of the ethylenediaminetetraacetate elution in a quantitative manner.

Although hydroxyethylethylenediaminetriacetate proved unsatisfactory for the separation of adjacent rare earths, it has been used successfully for separating scandium from the rare earths. Care must be exercised in recovering scandium, since it does not precipitate as the oxalate in the presence of complexing agents like citrate, ethylenediaminetetraacetate and hydroxyethylethylenediaminetriacetate. We found it expedient to evaporate our eluate solution to dryness and to destroy the chelating agent by ignition.

2. The Separation of Isotopes by Ion-Exchange (F. H. Spedding and J. E. Powell)

2.1 Separation of C^{12} and C^{13}

Preliminary investigations on the elution of formate ion down an acetate-cycle anion exchanger with hydrochloric acid showed some enrichment of C^{13} .

2.2 Separation of N¹⁴ and N¹⁵

Using three 10-foot long, 30-inch diameter, stainless steel columns, it has been possible to obtain a 30-fold enrichment of a sizeable amount of N¹⁵ (from .365% to 12%) by eluting an 8-foot long band of adsorbed NH₄⁺ down 320 feet of resin bed on this system.

3. Rare Earth Metallurgy (F. H. Spedding and A. H. Daane)

3.1 Preparation of Rare Earth Metals

Rare earth metals prepared by methods developed at the Ames Laboratory are very pure, in general, but are known to contain a small amount of tantalum, calcium, nitrogen and carbon. Small amounts of hydrogen and oxygen are also thought to be present, but are not known with certainty due to a lack of good analytical methods in these cases. In a program of improving the methods of preparing the rare earth metals, progress has been made in reducing the amounts of these impurities present in the metals.

It had been observed that, when exposed to air, the rare earth fluorides rapidly adsorbed considerable quantities of gases, and, even when handling time was reduced to a minimum, considerable amounts of adsorbed gases were found to be released when these fluorides were heated in a vacuum. This was also found to be true of the calcium metal used in the reductions. Such gases were obvious sources of such impurities as hydrogen, nitrogen, oxygen and carbon in the rare earth metals.

To remove the gases, a furnace and loading device have been devised in which the fluoride and the calcium are vacuum degassed and then mixed in an inert atmosphere. The charge is placed in a hopper on the reduction furnace, and after the tantalum crucible is outgassed, the charge is added to the crucible through a tantalum funnel arrangement. As the reduction occurs and the products melt, more charge may be added until the reaction crucible is filled with molten metal and slag. This method of reduction has been used to prepare about 1.5 kg of rare earth metal in one loading, and because of the elimination of the adsorbed gases from the charge and the crucible, a distinct improvement in metal purity has been observed. Also, the amount of tantalum impurity in the metal has decreased to below the detectable limit, indicating that these non-metallic elements may be in some way responsible for the small amounts of tantalum detected in the rare earth metals prepared without degassing the charge and crucible.

Experiments have been carried out on a method of preparing rare earth metals in a semi-continuous reactor. The first reduction was moderately successful in that a good yield of metal was collected in the water-cooled mold, but a large portion of the slag drained off with the metal. A second step in this process is the vacuum casting of the product metal to remove the small amounts of calcium. This has been done using a tantalum crucible and a water-cooled copper mold, and the results are very encouraging; cold shuts were present on the surface of the casting, but were not so severe as to appear impossible to correct. In addition to improving the quality of the product metal, these operations offer the additional advantage that the tantalum consumed is reduced manyfold, as the tantalum parts would only have to be replaced after considerable use.

3.2 Properties of Rare Earth Metals

3.2.1 Lanthanum-Carbon Alloy System

Thermal analyses carried out on alloys between LaC and LaC₂ indicate a minimum in the solidus curve in this region. Because of the reactivity of these alloys, it has not been possible to examine their microstructures to see if this is due to the presence of a eutectic. Densities of LaC and LaC₂ have been calculated from x-ray data and are 5.876 gm/cc and 5.327 gm/cc, respectively. In addition, a sample of GdC has been found to have a body-centered cubic structure with $a = 8.30 \text{ \AA}$ and a density of 7.83 gm/cc.

Resistivity measurements made on a specimen of LaC₂ indicate that the resistivity has decreased from approximately 55×10^{-6} ohm-cm at room temperature to an extremely low value at 77°K.

3.2.2 Other Rare Earth Alloys

Specimens of La-Gd alloys have been prepared and x-ray diffraction patterns show:

Alloy	Structure
90% Gd-10% La	The normal hexagonal closest packed structure of gadolinium with slightly increased lattice constants, as one would expect by substituting lanthanum atoms for the smaller gadolinium atoms.
75% Gd-25% La	The structure of this alloy is uncertain but it does not appear to have the structure of either lanthanum or gadolinium.

Alloy	Structure
50% Gd-50% La	First results indicate the "double c axis" structure of the hexagonal form of lanthanum.

A sample of an alloy containing 85% La and 15% Y does not appear to have the lanthanum structure. This may be due to lack of equilibrium and specimens are being annealed for further study.

3.2.3. Vapor Pressure of Thulium

A preliminary measurement has been made of the vapor pressure of thulium and shows a value of 10^{-2} mm at about 850°C, with a heat of sublimation of about 55 kcal/mole.

3.2.4. Miscellaneous

In dissolving residues remaining in tantalum crucibles after casting rare earth metals, a material which is hexagonal with $a = 3.07$ Å and $c = 4.94$ Å has been identified as tantalum nitride. It is apparent that tantalum scavenges the nitrogen from the rare earth metal to form this nitride, as the rare earth metals that have been prepared by these techniques have a very low nitrogen content compared with those prepared in other containers.

A report (ISC-702) entitled "Some Physical-Metallurgical Properties of Scandium, Yttrium and the Rare Earth Metals" by K. W. Herrmann, A. H. Daane and F. H. Spedding is being distributed.

Abstract

In continuing effort to learn more about the nature of metals, the rare earth elements in particular, the crystal structures and precision lattice parameters of these metals were investigated. High purity metals were examined by powder, single crystal and back reflection x-ray diffraction techniques. All but four of the back reflection samples were prepared by distillation in high vacuum (approximately 2×10^{-7} mm. mercury). The back reflection examinations, by which very accurate lattice parameters can be determined, were considered necessary if quantitative comparisons of the properties of the rare earths are to be made. Although scandium and yttrium are not classified as rare earths, they were considered similar enough in their behavior to include them in this study. The crystal structures and lattice parameters of the metals investigated are given.

From the crystallographic data of scandium, yttrium and the rare earth metals, the mole-atomic volume, density, axial ratio and metallic radii were calculated for each element and then graphically compared. In addition to the expected variations in these properties throughout the series due to structure differences and the "lanthanide contraction", other irregularities were also observed. These cannot be satisfactorily explained at present.

Microscopic examinations of the distilled metals revealed strong evidence for the existence of twinning. Several photographs are presented.

Considerable confusion exists in the literature concerning the phase transformations exhibited by the lighter rare earth metals. To obtain further information concerning these phenomena, the transformation temperatures of pure lanthanum, cerium, praseodymium and neodymium were determined by investigating the electrical resistivities of these metals as a function of temperature. They were studied over the temperature range 20°C to approximately 20° to 100°C below their melting points. The data are presented in graphical form. The transformation temperatures and resistivity values of the metals at 25°C are given.

High temperature crystallographic studies still in progress have shown the intermediate phase of lanthanum to be f.c.c. with a lattice parameter of $a_0 = 5.31 \text{ \AA}$ at about 260°C. At present no definite information concerning the high temperature structures has been obtained.

4. Fused Salts Program

4.1 Transport Numbers in Fused Salts (F. R. Duke)

The transport number of the anion in mixtures of AgNO_3 and the alkali nitrates has been determined for some compositions. The transport number does not change markedly from that in the pure salts, in which it varies from .15 to .25 in going from lithium nitrate to sodium nitrate to silver nitrate. Thus, although the cations show strange transport behavior, the anion does not.

A new method for determining transport numbers in salts has been used. A porous plate is partly saturated with the fused salt and a current is allowed to flow. Changes in "concentration" or actual amount of salt in the vicinity of the electrodes are measured. The tendency to flow back and equalize the amount of salt throughout the plate is nullified by the capillarity of the porous plate. Thus, the method is the same as the Hittorf method in aqueous solution. Transport

numbers for silver in AgNO_3 agree well with those determined in the moving bubble cell. The transport number of Na^+ in NaCl determined by this method is between 1.9 and 2.0, indicating a complex cation in this salt. The rate of the reaction $\text{Cr}_2\text{O}_7^{2-} + \text{NO}_3^- \longrightarrow 2\text{CrO}_4^{2-} + \text{oxides of nitrogen}$ was measured. This acid-base reaction is first order in bichromate and second order in the catalyst, Pb^{++} . Nitrate is the solvent.

Apparatus was constructed to gain better precision on the solubility of water vapor in mixed fused alkali nitrate solvent. In the absence of Li^+ , water vapor is very insoluble in the salt. With 15 mole percent Li^+ , the water vapor solubility is readily measurable, and apparently H^+ and OH^- in some form are present at very low H_2O concentrations, while hydrates of Li^+ up to $\text{Li}(\text{N}_2\text{O})_4^+$ are present at higher Li^+ concentrations.

4.2 Solubility of Water in Fused Salts (J. D. Corbett)

The unusual reactivity of fused salt systems containing LiCl toward most metals appears to be due to the presence of dissolved water. Experimentation has shown that the water is removed only slowly by evacuation; at the same time smaller amounts of HCl are produced by hydrolysis. The effect of the addition of foreign salts on the rate of the hydrolysis is as predicted by general acid-base theory.

A workable method for the measurement of the equilibrium water vapor pressure over these melts has been developed, based on the decrease in pressure of a known amount of vapor when equilibrated with the fused salt. For ten grams of the mixture LiCl-KCl (55:45), typical solubilities at 480°C are as follows, expressed in microequivalents of dissolved water at the specified pressure: 4.1 mm, 17 μ equiv.;

<u>P</u>	<u>Sol.</u>
5.8	33
10.9	86
15.0	169

The solubilities are about 20% higher at 395°C . It is apparent that Henry's Law is not obeyed.

4.3 Complex Formation in Fused Salts (J. D. Corbett)

The large negative deviations found in many fused salt systems have often been attributed to the formation of complex ions. However, except for recent work with dilute solutions

in molten nitrates, direct evidence for the presence of such ions in these systems has been lacking. Electromotive force measurements in suitable concentration cells have been found to give information concerning this type of interaction. With the cell



it is possible to measure directly the complexing of nickel by fluoride ion relative to that by the chloride ion of the solvent. The cell is contained in a constant-temperature-zone Marshall furnace under an inert atmosphere, using a fine grade sintered-glass disk as the diaphragm. Spurious stirring effects and a slow drift in the potential with time have been eliminated by sealing the electrode into glass beneath the surface of the salt.

In the analysis of the data, the transport number of the nickel in the presence of the large excess of solvent has been assumed to be negligible. At 500°C, with one mole percent nickel chloride throughout, nickel activities of 0.970, 0.940 and 0.927 (relative to the pure chloride solvent) have been obtained in the presence of 1.0, 2.0 and 3.0 mole percent fluoride, respectively. The effect of temperature on the relative activities is quite small. The data are being analyzed in terms of the possible equilibria involved.

4.4 Electrical Conductance Studies (F. R. Duke)

A report (ISC-686) entitled "Temperature Coefficient of Electrical Conductivity in the System Potassium Chloride - Zinc Chloride" by R. A. Fleming and F. R. Duke is being distributed.

Abstract

The phase diagram of the system KCl-ZnCl_2 has been constructed. Values of specific conductivity and density have been determined at eight temperatures in the range 475-650°C for a series of compositions covering the concentration range. From these data, equivalent conductivities were calculated. The temperature coefficient of conductivity as expressed by the activation energy of ionic migration was calculated at four temperatures for each mixture.

The phase diagram indicates compound formation in the solid state with the compound 2KCl-ZnCl_2 melting at about 450°C. Density isotherms are "S" shaped, deviating

from additivity in a positive direction at low concentrations of potassium chloride and exhibiting a slight negative deviation at high concentrations of potassium chloride. Isotherms of equivalent conductivity are approximately additive in the range $0.00 < X_{\text{KCl}} < 0.30$ but then begin to deviate negatively, reaching a maximum negative deviation near $X_{\text{KCl}} = 0.71$. The activation energy at constant temperature falls rapidly from that of zinc (II) chloride as the concentration of potassium chloride increases until X_{KCl} has reached 0.30. The activation energy then slowly falls to the limiting value for pure potassium chloride in an approximately linear manner.

The deviations noted in the isotherms of equivalent conductivity agree with the predictions of Bloom and Heymann [H. Bloom and E. Heymann, Proc. Roy. Soc. (London), A188, 392 (1946)]. A knowledge of the transport numbers of the individual ions is necessary for meaningful interpretation of the isotherms of activation energy.

4.5 Metal-Metal Salt Solubilities (J. D. Corbett)

Examination of other systems for metal-metal salt interaction has further confirmed the hypothesis that, among the post-transition representative elements, solution of a metal in its normal halide is due to the formation of a lower oxidation state of that halide. Additional solubilities that have been measured are shown in Table 1.

Table 1

System	Solubility mole % metal	Temperature
Zn-ZnCl ₂	0.18	500
	1.64	700
Zn-ZnI ₂	3.7	600
Sb-SbCl ₃	0.02	275
Sb-SbI ₃	0.3	200
	6.4	400
	7.1	475
Ga-GaBr ₂	4	170
Co-CoI ₂	ca. 2	670

The metal-saturated zinc chloride and antimony iodide systems are diamagnetic; the ZnCl_2 , ZnI_2 , SbCl_3 and GaBr_2 solutions are colorless. Although such systems usually yield finely divided metal when they solidify, the Zn-ZnCl_2 solution at 500°C gives a colorless glass when quenched. On heating the glass, the salt is observed to crystallize at 125°C , while the blackening characteristic of the metal appears rather sharply at 180°C .

The nature and extent of the solubilities in the systems are strongly indicative of the presence of subhalides therein, these being of such borderline stability that they cannot exist as pure phases, but only when dissolved in the normal salt. The trends both within the groups, and upon variation of the halide ion are as expected for this type of interaction. In the Ga-GaI_2 system, where the metal solubility is 40.5%, the subhalide is of sufficient stability that it can be isolated.

It is also to be noted that in this region of the periodic table there is a direct correspondence between the systems that show transport of the heated metal by the gaseous normal halide (presumably as a subhalide), and those in which significant solubility of the metal in the liquid salt is observed at a comparable temperature. It therefore appears as if there is a direct relationship between the two phenomena.

5. Thermistor Studies (J. D. Corbett)

A paper entitled "The Use of Thermistors in Cryoscopic Measurements" by R. K. McMullan and J. D. Corbett (ISC-676) has been submitted for publication in J. Chem. Educ.

Abstract

The applicability of thermistors to cryoscopic measurements has been examined. A simple Wheatstone bridge was used to measure the temperature-sensitive resistance of the thermistor. Theoretical equations directly relating thermistor resistance at the freezing point to the concentration of the solution have been developed. Data obtained in benzene or 1,4-dioxane with concentrations of phenanthrene or naphthalene up to a mole fraction of 0.008 fit the equations presented with a standard deviation corresponding to about one millidegree. Measurements in pyridine at -42° , where a Beckmann thermometer cannot be used, gave comparable results. Values calculated for the heats of fusion of the solvents benzene, dioxane and water agreed quite well with those reported in the literature. Simplified resistance-concentration equations that gave essentially the same results have also been suggested.

Results obtained simultaneously with a thermistor and a Beckmann thermometer indicated that the method gave results with about one-third the uncertainty of the usual Beckmann technique. Observations on the stability of thermistors are presented.

6. The Lower Oxidation States of Gallium (J. D. Corbett)

The molecular weights of gallium(II) chloride in anhydrous benzene and 1,4-dioxane have been measured by means of a thermistor. The compound is dimeric (Ga_2Cl_4) in benzene at infinite dilution, and polymerizes slowly as the concentration is increased. A new method for the analysis of such data in terms of the concentrations of the various species is being developed, based on a direct mathematical solution instead of the usual successive approximation methods. Up to 0.16 molal, only dimer, tetramer and hexamer are indicated. In dioxane, GaCl_2 is dimeric up to 0.03 molal.

The reactions of GaCl_2 in benzene and dioxane with various bases are being examined. Pyridine reacts with benzene solutions to give primarily $\text{GaCl}_3 \cdot \text{Py}$ and a solid which is probably a mixture of metal and GaCl . In the more basic dioxane, the principle product is a moderately soluble pyridine complex of Ga_2Cl_4 , with only small amounts of GaCl and $\text{GaCl}_3 \cdot \text{Py}$ resulting from a side reaction.

The dielectric constants of benzene solutions of GaCl_2 have been measured, using a Sargent Oscillometer with a cell compensator. Densities were measured with a quartz-fiber magnetic balance. By the usual extrapolation to infinite dilution, a dipole moment of 15 to 17 D was obtained for Ga_2Cl_4 . This strongly suggests the existence of the ion pair $\text{Ga}^+ (\text{GaCl}_4)^-$ in the solution, and not $\text{Cl}_2\text{Ga}-\text{GaCl}_2$. The stronger solvation by dioxane apparently has considerable effect in reducing ion-pair aggregation in that solvent. Although such aggregation is observed in benzene, the rather high solubility of the salt (2 mole percent) must indicate a fairly specific Ga^+ benzene interaction.

7. The Chemistry of Gallium(II) Halides in Aqueous Base (J. D. Corbett)

The slow and homogeneous evolution of hydrogen from solutions of the gallium dihalides in 1 to 4 molar NaOH has been used to follow the kinetics of the oxidation. The reaction is initially first order in reduced gallium and in hydroxide, and zero order in gallium(III) and in iodide ion. A change in the kinetics toward the end of the oxidation indicates the reaction is somewhat complex. Upon neutralization of these solutions the reducing strength is completely precipitated as hydrous oxide.

Kinetic examination of GaI_2 and $\text{GaI}_2\text{-GaI}$ solutions in base shows these reactions to be considerably slower. Since the dielectric measurements in benzene indicate the presence of Ga^+ in the dichloride, the observed independence of the reaction rates on Ga(III) and I^- concentration would lead one to expect

the same kinetics with $\text{Ga}^+ (\text{GaI}_4)^-$. The presence of another oxidation state in the iodide, i.e., Ga(II) , is one explanation. An extensive study of the reactions of basic solutions of GaCl_2 and GaI_2 with foreign ions also appears to indicate the presence of a stronger reducing agent in the iodide system.

8. Conductivity in Ion Exchange Resin (F. R. Duke)

A paper entitled "Electrical Conductance Studies on An Ion Exchange Resin" by R. P. Puri, F. R. Duke, and June Lomnes was submitted to ISC-J. of Sci.

Abstract

The relative conductivity of univalent ions in an exchange resin compared to that in aqueous solution indicates that the ions have similar hydration and mobility in the two media. This is further bolstered by the effect of changing solvent on the conductivity. The energy of activation for conductance indicates that the bivalent ions are as loosely held to the resins as the univalent ions, but that steric factors greatly reduce the conductivity of the bivalent ions.

9. Reaction Kinetics (F. R. Duke)

A paper entitled "The Kinetics of the Ce(IV) - Ce(III) Exchange Reaction in Perchloric Acid" by F. R. Duke and F. R. Parchen was submitted to J. Am. Chem. Soc.

Abstract

The rate of the Ce(IV) - Ce(III) exchange reaction is found to be first order in Ce(III) , first and second order in Ce(IV) and complex order in $[\text{H}^+]$. At high acidities, the Ce(IV) and $[\text{H}^+]$ dependencies are best explained by the reaction of Ce(III) with the species Ce(OH)_2^{+2} , Ce(OH)_3^+ , and $[\text{CeO} \cdot \text{CeOH}]^{+5}$. At low $[\text{H}^+]$ more highly hydrolyzed and polymerized species appear to be involved.

10. Adsorption Studies (R. S. Hansen)

Experimental work on the activities of components in the systems acetic acid-perfluoroacetic acid, propionic acid-perfluoropropionic acid, and butyric acid-perfluorobutyric acid was completed. Systems of the type $C_n H_{2n+1} COOH - C_n F_{2n+1} COOH$ are interesting in the theory of solutions in that they represent binary mixtures of molecules comparable in size (an ideal feature) which however associate (a non-ideal feature) in such a manner that molecules of either component should have the same number of association partners (a simplifying feature). These systems are, therefore, intermediate in complexity between ideal and semi-ideal systems such as hydrocarbon and hydrocarbon-fluorocarbon mixtures and complex aqueous-alcohol systems. A statistical treatment of the system $C_n H_{2n+1} COOH - C_n F_{2n+1} COOH$, assuming aggregation limited to dimerization, was developed.¹ Experimental data were rather well represented by this treatment, and in particular were well represented if the total monomer concentration was assumed negligible. Under these circumstances, the adjustable constant characterizing the association equilibrium is of the form

$$K = \frac{[HF]^2}{[H_2][F_2]}$$

in which H_2 is the hydrocarbon acid dimer, F_2 the fluorocarbon acid dimer and HF the cross dimer. The values of K best representing the data were in all cases satisfying, close to similar constants obtained by direct measurement of the comparable equilibrium in the gas phase.

11. Heat Capacity Measurements (L. D. Jennings and F. H. Spedding)

The heat capacity of anhydrous chromic chloride and of holmium from 15°K to 300°K was measured. The results are shown in Figs. 1 and 2. At 300°K the entropy of chromic chloride is $29.52 \pm .07$ e.u. and $(H^\circ - H^\circ_0)/T$ is $14.19 \pm .03$ e.u. At 300°K the entropy of holmium is $18.27 \pm$ e.u. and $(H^\circ - H^\circ_0)/T$ is $6.421 \pm .010$ e.u.

The value for the entropy of holmium at 300°K may be compared with that of 17.83 e.u. predicted on the basis of the following simple assumptions: 1. The conduction electron contribution to the entropy is constant throughout the rare earth elements. 2. The lattice heat capacity is given by a Debye function for which the Debye temperature varies linearly through the rare earth series. 3. The bound electron contribution is given by

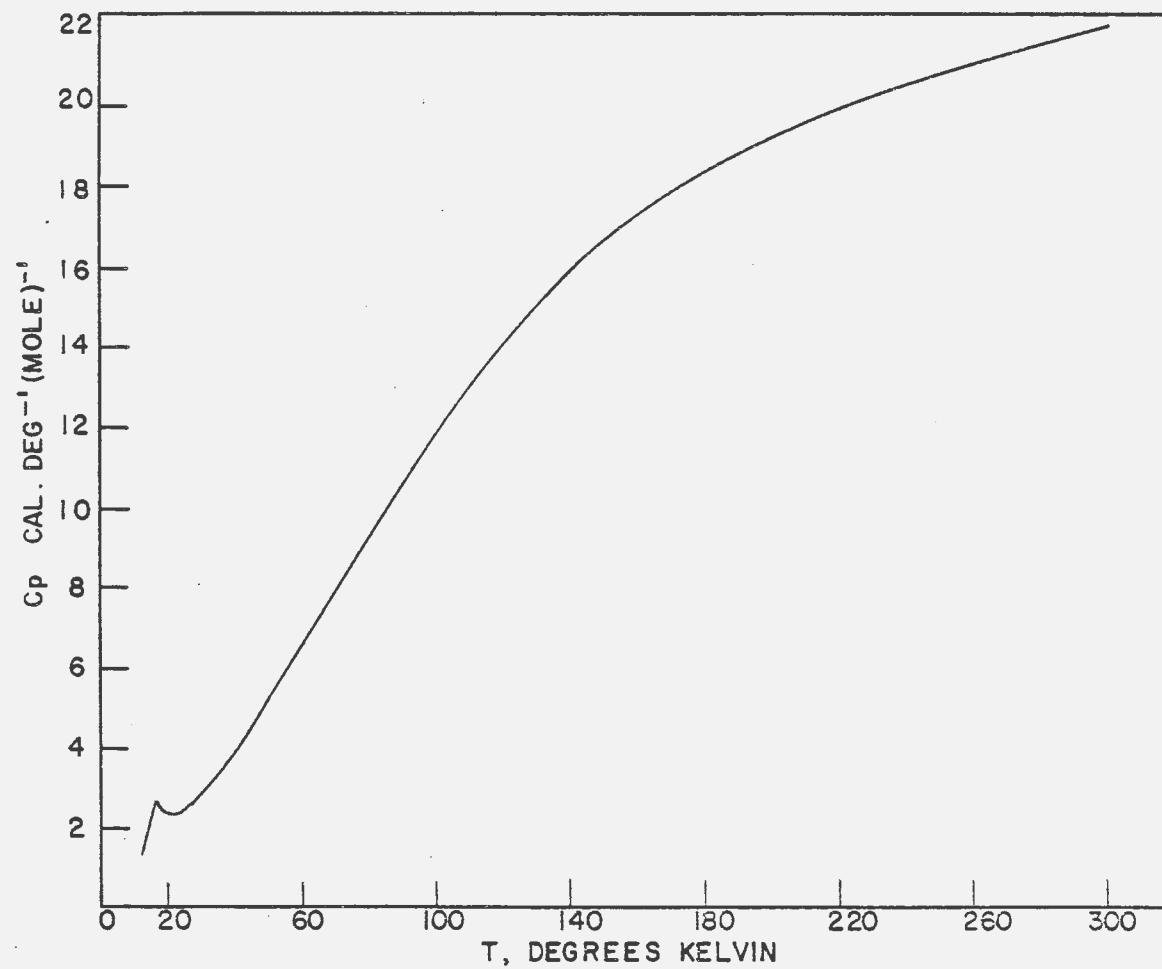


Figure 1. Heat Capacity of Chromium Chloride.

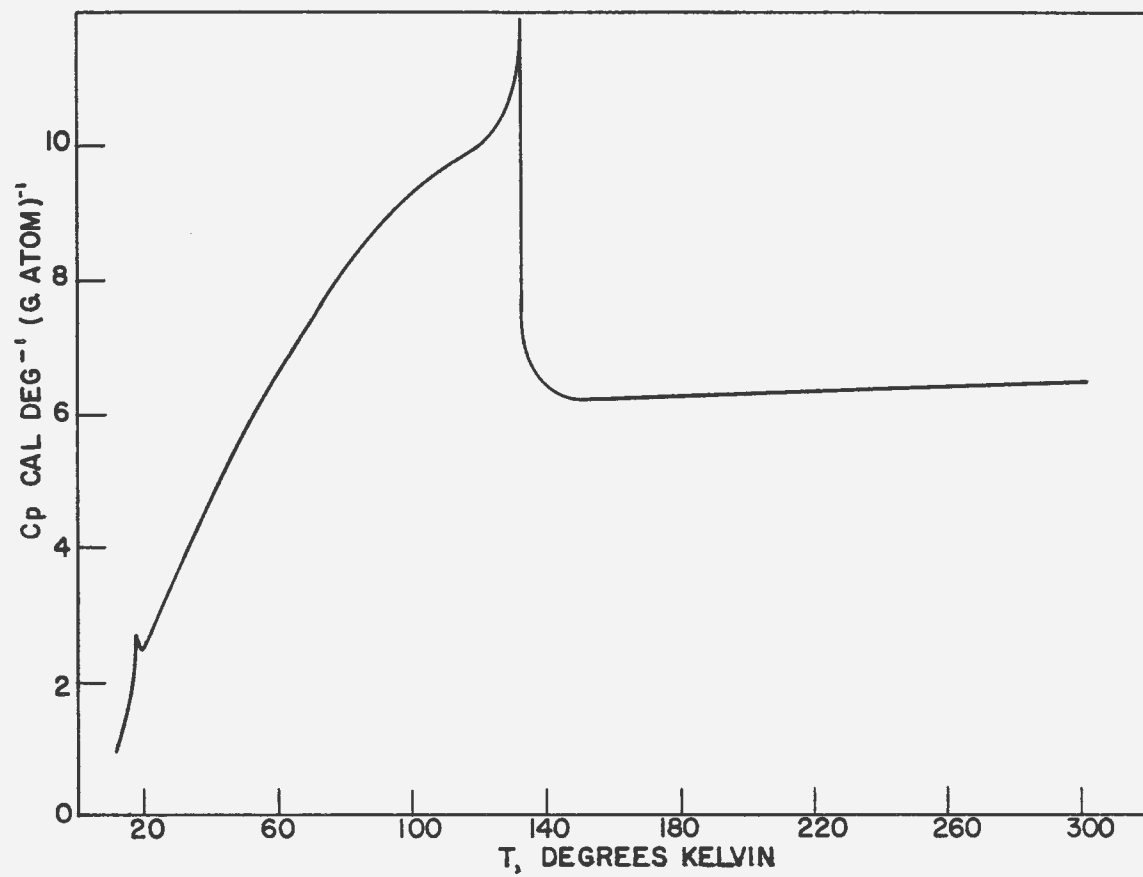


Figure 2. Heat Capacity of Holmium.

$R \log(2J+1)$ where J is the value appropriate to the tripositive ion. The last assumption is valid if the bound electron spin has $(2J+1)$ available states with equal probability of occupation at 300°K. These assumptions predict the entropy within experimental error for dysprosium and erbium, the two neighbors of holmium in the periodic table. That the assumptions give a result two percent in error for holmium calls for a re-evaluation of the assumptions.

12. Pyrolysis of Toluene (L. D. Jennings)

The (C-H) bond dissociation energy in the methyl group of toluene has been studied. Pyrolyses have been carried out, extending the work of M. Szwarc [M. Szwarc, J. Chem. Phys. 16, 128 (1948)] to lower temperatures (to 705°C). Assuming the mechanisms postulated by Szwarc, we obtain the points shown on the graph in Fig. 3 of the logarithm of the rate constant versus the reciprocal temperature. The solid line is given by a least squares fit and yields an activation energy of 78.3 kcal/mole. The dotted line gives greater weight to the low temperature points and yields an activation energy of 84 kcal/mole. Szwarc's value is 77.5 kcal/mole. Our value is, however, lower than that of 89.9 kcal/mole obtained by H. Anderson, et al. [H. Anderson, Jr., et al., J. of Chem. Phys. 21, 1258 (1953)] using bromination kinetics.

13. Gas Analysis by Mass Spectrometry (H. J. Svec)

Vacuum fusion of some metals produces mixtures of CO, N₂ and H₂. A mass spectrometric method was developed for analyzing these mixtures involving the measurement of the 29⁺/28⁺ ratio, the intensity of the 28⁺ beam and the intensity of the H₂⁺ beam. Both N₂ and CO have about the same relative ionization efficiency for 70 volt electrons. In order to place analytical results on an absolute basis, a correction factor of 4.290 must be applied to the H₂⁺ peak intensity to account for the different ionization efficiency compared to that of N₂. Table 2 shows analyses of CO-N₂ mixtures.

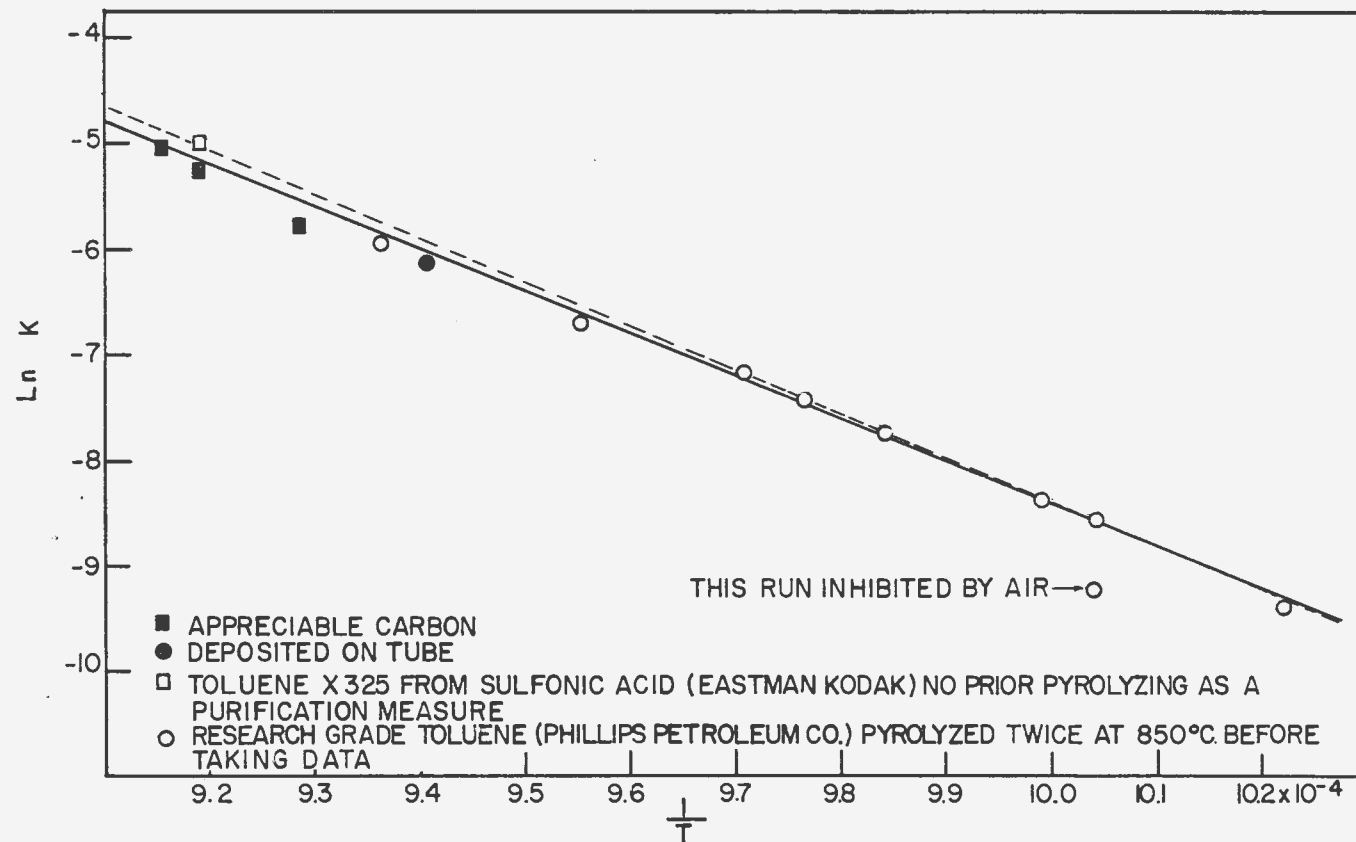


Figure 3. Pyrolysis of Toluene.

Table 2
CO-N₂ Mixture from 29/28 Ratios

Sample	% N ₂ (mixed)	% N ₂ (mass spectr.)
1	7.00	6.56
2	15.23	14.80
3	30.86	31.14
4	60.49	60.50
5	83.24	83.60
6	89.20	89.25

14. Kinetics of Metal-Water Vapor Reactions (H. J. Svec)

When thorium reacts with water vapor, ThO₂, H₂ and ThH₂ are formed. In the Ca-water vapor reaction only Ca(OH)₂ and H₂ have been positively identified as reaction products. The kinetics of both reactions follow a logarithmic rate law.

Research has begun on the Mg-water vapor reaction. The reaction is very slow, the rate being unmeasurable, by our technique, below 475°C. Only MgO and H₂ are positively identified as products. The rate law is linear.

15. Preparation and Mass Spectra of N₂²⁹ (H. J. Svec)

This molecular species of nitrogen may be prepared by the thermal decomposition of NH₄NO₂. Work with 60% N¹⁵ NH₄⁺ salts and 99.99 atomic percent N¹⁴NaNO₂ has proved that N₂ is formed primarily by the combination of the NH₄⁺ nitrogen atom with that of NO₂⁻. We have prepared N₂²⁹ from the highest N¹⁵ preparation we had available in quantity and have produced nitrogen which is 97.2% N₂²⁹, 2.8% N₂²⁸ and 0.02% N₂³⁰. The mass spectra of this material indicate the following relative amounts of ion fragments for 75 volt electrons:

N ₂ ²⁹⁺	1000.0
N ₂ ²⁹⁺⁺	27.2
N ¹⁴⁺	7.1
N ¹⁵⁺	8.7

These data are corrected for the N_2^{30} and N_2^{28} in the sample. N_2^{29} may be kept for several days with no great disproportionation being observed.

Pyrometallurgy

1. Metallurgical Separation of Fuel and Fission Products (A. F. Voigt)

Work was continued on extraction of artificial "fissium" mixtures with silver, cerium and lanthanum and the subsequent treatment of the extractant layer after original extractions with silver.

In the extraction studies the most important fission products, namely zirconium, molybdenum, ruthenium and representative rare earths, were present in the mixture. Accumulated results of many experiments with silver, cerium and lanthanum extractants show that molybdenum is not removed by any of these extractants, that the rare earths are largely removed by all of them and that the extraction of zirconium is in the range of 40-75 percent complete. A very interesting result is the behavior of ruthenium which is not extracted at all by silver but which extracts in a fairly high percentage into the rare earth extractants, particularly cerium.

Experiments were conducted to find out whether equilibrium was being reached or approached in these extractions. In these experiments portions of the extractant metal phase were taken for analysis and the remainder was re-extracted with uranium. In most cases the observed extraction coefficients (conc. in extractant phase/conc. in U) for the reverse extractor were larger than those for the forward extraction by factors of 2 to 100, indicating that considerably longer extraction periods would be necessary in order to reach equilibrium.

Another set of experiments was designed in order to determine whether that portion of the various fission products which remains in the uranium in one extraction can be removed by repeating the extraction. In most cases, within the experimental error, the second extraction duplicated the results of the first. Thus, it was indicated that continuous extraction processes or repeated batch processes could be developed.

A study is also being made of different procedures for treating the extractant phase, after it has extracted the fission products and plutonium, in order to remove these materials from it and render it acceptable for reuse.

Most of these studies have been concerned with silver as the extractant metal and, to date, have been confined to the fission products. Those fission products removed by volatility are not present in the silver layer, nor are those like molybdenum and ruthenium whose extraction coefficients into silver are very small. Consequently, we have studied the fission products that are appreciably extracted into silver, namely zirconium and a rare earth, which, in these experiments, is cerium.

Several techniques of removing these fission products from silver have been studied. Electrorefining of the silver using a molten salt bath has proven to be a useful technique but there are a number of drawbacks. The silver deposit at the cathode is dendritic and traps the electrolyte so that a clean separation of metal and salt after cooling is difficult. However, in spite of these difficulties, the process of electrically dissolving the silver at the anode, using a silver chloride bath, and re-depositing pure silver at the cathode appears to give good decontamination--at least in the initial stages of the electrorefining. In three runs in which cerium was the only fission product present, the decontamination factors obtained were 25, 82 and 102, corresponding to 96, 98.8 and 99 percent removal of the cerium.

A somewhat simpler technique which appears to be satisfactory is fused salt extraction from molten metal. The majority of the fission products, particularly those which would be extracted into silver, are more readily oxidized than silver and consequently would go into a salt layer in the presence of an oxidizing agent. Silver chloride is a good oxidizing agent for this purpose. Experiments have been run using various mixtures of silver and sodium chlorides as extractants. A total of 23 such experiments with cerium and zirconium tracers are summarized in the following table. In each experiment approximately 5 gram samples of silver containing tracer and carrier cerium and zirconium were heated with an equal volume of salt to 100°C for 30 minutes. They were not stirred.

Table 3 shows the type of distribution and removal obtained. The distribution coefficient is the ratio of fission product in the salt phase to that in the silver phase and the decontamination factor is the ratio of fission product in the original silver to that in the silver after extraction.

It can be seen that in the presence of even 10% AgCl the removal of these fission products from silver is nearly complete, while, without any silver chloride present, it only reaches the 60-90% range.

Table 3

Second Step Extraction Runs - Ag vs AgCl-NaCl

	Decontamination Factor		Distribution Coefficient	
	Ce	Zr	Ce	Zr
AgCl	V		G	
9% NaCl	U	U	F	F
47% NaCl	V	X	G	G
90% NaCl	V	X	H	H
NaCl	S	T	D	F
Blank	Q	P		
Code				
	D.F.	% Removed		K _d
P	1-1.3	0-23	D	0.3-3
Q	1.3-1.8	23-45	F	30-100
S	2.5-5	60-80	G	100-300
T	5-10	80-90	H	300
U	10-50	90-98		
V	50-200	98-99.5		
X	400	99.75		

A paper entitled "Liquid-Metal Extraction for Processing Spent Fuel" by A. F. Voigt, A. H. Daane, E. H. Dewell, R. G. Clark, J. E. Gonser, J. F. Haefling, and K. L. Malaby was submitted for publication.

Abstract

Plutonium and the fission products can be removed from irradiated uranium by liquid-metal extraction using

another metal, immiscible with uranium. Metals studied have been silver, cerium and lanthanum. Plutonium removal by silver is high, by the rare earth metals moderate. In all cases volatile elements, including cesium, strontium and barium, are removed. Rare earths are efficiently removed. Ruthenium and molybdenum are largely unaffected. Experiments with synthetic fuels corresponding to long burn-up periods show improved removal of most elements. Repeated batch extractions indicate that a continuous process could be developed, separating the fuel into uranium, plutonium and fission product fractions.

2. Alloy Studies (A. H. Daane)

The procedure for preparing "fissium" (synthetic spent reactor fuel) has been altered in an attempt to obtain a more homogeneous product. A concentrated alloy is first prepared by arc melting the uranium with the fission product metals. This is then diluted to the final concentration by melting in a 2" diameter crucible in which the stirring by the induction field was improved. The 2" diameter specimen is then cast into a 1" diameter crucible to give the final product. Analyses show the material to be homogeneous with respect to all elements except zirconium which has been concentrated toward the top of the melt, probably as a result of liquation of zirconium carbide.

The liquid immiscibility limits of uranium and samarium metals have been studied with the results given in Table 4.

Table 4

Uranium-Samarium Metal Liquid Immiscibility Limits

Temperature, °C	U in Sm Layer	Sm in U Layer
1132	1.1 \pm 0.1 wt. %	0.10 to .15 wt. %
1140	0.9 \pm 0.02	0.17 \pm 0.01
1200	1.0 \pm 0.05	0.16 \pm 0.02
1210	0.9 \pm 0.02	0.23 \pm 0.03
1225	1.0 \pm 0.10	0.25 \pm 0.03

3. Corrosion Studies (A. H. Daane)

A tantalum loop (described in ISC-614) in which a liquid 95% Bi-5% U alloy was circulated for several thousand hours at over 900°C was examined at several points for evidence of corrosion. Our findings may be summarized as follows:

1. There was little or no evidence of attack of the tantalum by the liquid metal.
2. There was evidence of oxidation of the UBi_2 crystals as a considerable amount of this phase (oxidized UBi_2) was found on the surface of the liquid reservoir chamber where it had floated during operation of the loop. The UBi_2 phase apparently oxidizes extremely rapidly, both at high temperature and at room temperature.
3. Incomplete x-ray diffraction studies indicate UBi_2 may have an orthorhombic structure.
4. At several points where the tantalum loop was in contact with its inconel jacket, attack of these metals on each other was observed. X-ray diffraction studies of material from these areas indicate a possible tantalum-nickel carbide as the main constituent present.

Analytical Chemistry

1. Analytical Procedures (C. V. Banks)

1.1 Antimony

A method was developed for the determination of antimony in hydrochloric acid solutions containing both iodide and free iodine. Hypophosphorous acid was used to reduce both the antimony and free iodine in boiling 1:1 hydrochloric acid solution. After dilution, the antimony was titrated with a standard iodine solution.

1.2 Cobalt and Nickel

Cobalt and nickel were determined by a method developed for solutions containing both cobalt and nickel thiocyanates. The total cobalt and nickel in an aliquot was titrated with enta (ethylenediaminetetraacetic acid) using dithizone as an indicator. The cobalt from a second aliquot was then extracted into chloroform with α -nitroso- β -naphthol and the remaining nickel was titrated with a standard solution of enta.

1.3 Fluorine

Fluorine was determined in vanadium(III) fluoride by an adaptation of the Warf, Cline and Tevebaugh (J. C. Warf, W. D. Cline and R. D. Tevebaugh, Anal. Chem. 26, 342, Feb. 1954) pyrohydrolysis technique. It was found necessary to change the pyrohydrolysis temperature to 700°C to prevent sublimation of vanadium(III) fluoride.

The pyrohydrolysis rates of lanthanum, yttrium, neodymium, praseodymium, and cerium trifluoride were studied. The fluorides were all pyrohydrolyzed at 900 to 950°C. The hydrofluoric acid was titrated as it was evolved. Cerium(III) fluoride seemed completely pyrohydrolyzed after 30 minutes but only 94.6 percent of the theoretical amount of fluorine was recovered. For neodymium, 101 percent of the theoretical amount of fluorine was recovered in 40 minutes. Yttrium yielded 96.9 percent of its fluorine in 35 minutes, then very slowly evolved more hydrofluoric acid. The praseodymium curve was similar to the neodymium curve. Lanthanum, however, was pyrohydrolyzed very slowly and was still giving up hydrofluoric acid after 210 minutes.

1.4 Iodine

Total iodine was determined in hydrochloric acid solutions containing antimony, iodide and free iodine by oxidizing the samples with cerium(IV) sulfate, extracting the iodine into chloroform, and then titrating the chloroform phase with standard thiosulfate.

1.5 Magnesium

A method was devised for separating magnesium from yttrium, thorium, and aluminum. The yttrium, thorium and aluminum are complexed with enta at pH 4.5. Magnesium does not form a complex at this pH. The solution is then passed through a column containing a cation exchange resin. The magnesium is retained and the complexed metals pass through. The magnesium can then be removed with hydrochloric acid.

1.6 Titanium

A procedure for the determination of trace amounts of titanium in niobia was completed. The useful range is from 15 to 500 ppm of titanium dioxide in niobia with a precision of ± 30 ppm. Qualitative interference studies indicate strong interference from tantalum, vanadium, chromium and molybdenum. No interference from zirconium was observed.

1.7 Vanadium

It was found that the present amount of vanadium in vanadium(III) fluoride can be measured by removing the fluoride by fuming with sulfuric acid, then oxidizing vanadium(III) to vanadium(V) with potassium peroxydisulfate. The vanadium(V) can be quantitatively titrated with iron(II) using ferroin as the indicator if done in strong acid media.

1.8 Water

Water was determined in vanadium(III) fluoride by the Karl Fischer titration; the samples are dissolved by prolonged shaking in a closed system with absolute methanol.

1.9 Zinc

A method was devised for the determination of zinc in yttrium metal by a polarographic procedure using thallium as an internal standard.

Zinc was determined in uranium-bismuth-zinc alloys by an anta-titration after removing all the bismuth and most of the uranium by a double ammonia precipitation. Small amounts of uranium do not interfere in the titration.

2. Titration of Sulfate Ion (J. S. Fritz)

A method has been developed for determining relatively small quantities of sulfate in the presence of a large excess of other metal salts. The sulfate is separated from chloride, nitrate, perchlorate and from most metal ions by means of a small column of activated alumina. In the proposed method, an acid solution of the sample is passed through an alumina column in the chloride or perchlorate form. All of the sulfate present in the sample is taken up by the column; a small fraction of the other anions is also taken up. After washing, the sulfate is eluted from the column with dilute ammonia. The eluate is then passed through a cation exchange column in the hydrogen form and the sulfate is titrated with 0.01 M barium perchlorate according to the method of Fritz and Yamamura (Anal. Chem., 27, 1461 (1955)).

This method has been used to determine sulfate in samples containing as little as 0.5 ppm of sulfate; also in chloride-sulfate mixtures containing as little as 0.02 mole percent sulfate. Small amounts of sulfate in metal salts can be determined except in those cases where the metal ion forms a slow-reacting sulfate complex. The alumina column will quantitatively

separate sulfate from Zr(IV) or Cr(III) if the metal ion is first complexed with Entol (N-hydroxyethylethylenediamine-triacetic acid).

A report (ISC-667) entitled "I. Direct Titration of Sulfate. II. High Precision Spectrophotometric Analysis" by M. Q. Freeland and J. S. Fritz is being distributed.

Abstract

A method is proposed in which sulfate is titrated directly with standard barium solution. The end point is indicated by the adsorption of Alizarin Red S or Thorin onto the barium sulfate with a distinct color change from yellow to pink. The sulfate sample must contain 30 to 40% methanol for these indicators. Coprecipitation errors are greater than for gravimetric sulfate methods, but most of these can be avoided by the preliminary removal of cations with an ion exchange column. In the absence of interfering anions the ion exchange-titrimetric method is as precise as the gravimetric method and considerably faster.

A complete review of literature on titrimetric sulfate determination is included with bibliography. The experimental work leading to the proposed method is detailed and discussed.

Optically matched cuvettes are necessary for existing high precision spectrophotometric methods. The maintenance of optical matching is not practical for routine analysis at high precision. Procedures are presented utilizing a modification of the Beer's law equation which permit the use of unmatched cuvettes for high precision spectrophotometric analysis. The errors brought about by the use of unmatched cuvettes are calculated and they indicate the optimum conditions, relative to mismatching, for the use of the existing methods.

These procedures were applied to the analysis for vanadium in three vanadium-aluminum alloys. The accuracy obtained on synthetic samples averaged 0.1%. The reproducibility on the actual samples averaged better than 0.2%.

3. Determination of Organic Acids (J. S. Fritz)

It was found that the individual constituents of many mixtures of organic acids can be differentiated quantitatively by an alkalimetric titration in non-aqueous solution. Acetone

or dimethylformamide is used as the solvent for the sample and a standard solution of N-triethylbutylammonium hydroxide in benzene-methanol is used as the titrant. Unlike most previous systems for non-aqueous titration of acids, these titrations can be followed very well using an ordinary pH meter equipped with ordinary glass and calomel electrodes.

4. Titration of Mercury (J. S. Fritz)

A paper (ISC-661) entitled "Titration of Mercury with Bis(2-hydroxyethyl)dithiocarbamate" by J. S. Fritz and S. A. Sutton was submitted for publication to Anal. Chem.

Abstract

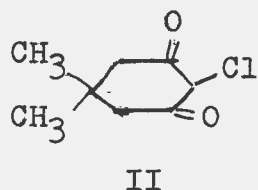
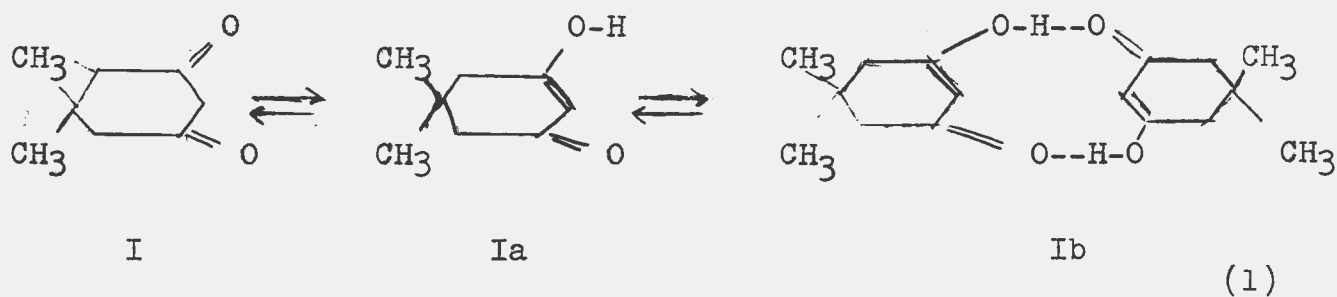
A direct titrimetric method for mercury(II) has been developed which permits the determination of mercury in the presence of chloride, bromide, and numerous metal ions. The mercury is titrated with a standard dithiocarbamate solution in the presence of ethylenediaminetetraacetate and copper(II). Although most mercury dithiocarbamates are insoluble, formation of a precipitate is avoided by using bis(2-hydroxyethyl)dithiocarbamate as titrant and acetone-water as the solvent for the mercury. The end point of the titration is indicated by the appearance of a yellow color caused by reaction of the first excess dithiocarbamate with copper(II). The titration may also be followed potentiometrically using a silver-dithiocarbamate indicator electrode.

5. Service Analyses (C. V. Banks)

A total of 3,270 service analyses were made during the period of this report.

6. Properties of β -diketones and Their Chelates (G. S. Hammond)

More studies of the absorption spectra of enolizable diketones and their metal derivatives have revealed interesting and suggestive facts. We have carried out a careful comparison of cyclic and acyclic compounds and the data are summarized in Table 5. It is found the DPM (dipivaloylmethane) and acetyl-acetone have spectra which are nearly invariant in various solvents with the exception of water. On the other hand, methone, I, and 2-chloromethone, II, show wide variation in their spectra.



These variations can be accounted for by a reasonable set of hypotheses. The acyclic diketones are largely represented by Eq. 2 as equilibrium mixtures of cyclic enol and acyclic diketo forms.

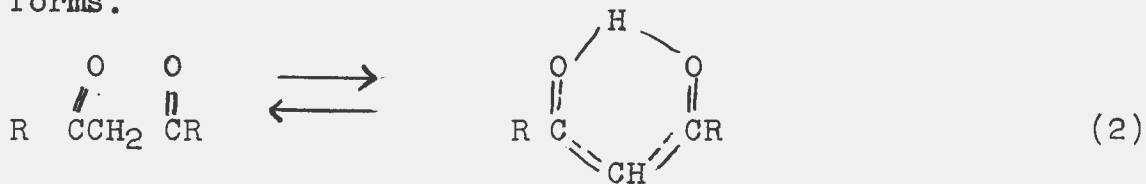


Table 5

The Ultraviolet Absorption Spectra of Some β -diketones

Compound	(m_{\max})	\max ($\times 10^{-4}$)	Solvent
DPM	275	1.2	cyclohexane
DPM	275	1.1	ethanol
DPM	275	0.9	acetonitrile
DPM	277	0.2	water or dilute mineral acid.
DPM	290-1	0.4	6×10^{-2} M aq. NH_3

Table 5 (Continued)

Compound	(m_{\max})	\max ($\times 10^{-4}$)	Solvent
Acetylacetone	271	1.0	cyclohexane
Acetylacetone	273	1.0	ethanol
Acetylacetone	273	0.2	water or dilute mineral acid
Acetylacetone	291	2.2	4×10^{-3} M aq. NH_3
3-Methylpentane-2,4-dione	286	---	heptane
	288.5	---	ethanol
Methone	244	1.26	dimethylcellosolve
Methone	256	1.45	ethanol (shoulder 280-90 $m\mu$)
Methone	280.4	2.35	neut. aq. solution
Methone	280.8	2.68	aqueous alkali, pH ca. 10
Methone	258.2	1.65	aqueous acid, pH ca. 2
Methone	Very weak absorbance in UV region		cyclohexane
Chloromethone	290.7	2.34	neut. aqueous solution
Chloromethone	291.1	2.24	aqueous alkali, pH ca. 11
Chloromethone	269.8	1.38	aqueous acid, pH ca. 1-2
Chloromethone	254	1.4	methanol
Chloromethone	270	1.20	ethanol (shoulder 285-90)
Chloromethone	265.7	1.45	dilute ethanolic HCl (no shoulder)
Chloromethone	256	1.34	dimethylcellosolve
Chloromethone	249.5	(gradually disappears)	cyclohexane
Dichloromethone	213	0.1	cyclohexane

The strong ultraviolet absorption is almost exclusively due to enol and the varying intensity of the 275 m μ absorption peak reflects only the variation in the enolization constant with solvent properties. The spectra of the enols themselves are ~~essentially~~ invariant with solvent [G. Guter and G. S. Hammond, ISC-6737]. The cyclic diketones tend to be more highly ketonized in non-hydroxylic solvents since the hydroxyl groups, lacking the opportunity for internal hydrogen bonds, are stabilized by the presence of basic atoms in the solvent. In water both I and II are essentially completely ionized in dilute solutions and they are partially dissociated in ethanol. It is interesting to note that when enol of II, the stable crystalline form, is dissolved in cyclohexane, it is converted to the stable diketone form very slowly whereas the ketonization of I is very rapid. This behavior is attributed to the existence of a very tight, hydrogen-bonded dimer of II in even dilute cyclohexane solutions.

Preliminary studies of the halogenation of dimedone have been carried out since they may have supplemental value in aiding the interpretation of the halogenation of the metal chelates of DPM (vide infra).

7. Formation Constants of β -diketone Chelates (G. S. Hammond)

A report (ISC-673) entitled "Steric Effects on the Formation of Constants of Metal Chelates of Beta-Diketones" by G. A. Guter and G. S. Hammond is being distributed.

Abstract

Evidence is presented which indicates that chelating ability may be greatly altered by changing the steric requirements of the ligand. A series of formation constants was measured for three beta-diketones. Thermodynamic values could not be obtained but relative concentration constants were. The constants obtained were correlated with each other and with the basicity of the reagent toward a proton. Each correlation indicated that the formation constants for the copper chelates of diisobutyrylmethane and dipivaloylmethane were low and exhibited large separation factors. However, relatively small separation factors were found for metal chelates which do not form square planar complexes.

A simple method for determining the extent of enolization of beta-diketones and the kinetics of enolization is presented. The method makes use of spectrophotometric measurements in the ultraviolet region. Correlations were observed between the pKa of the chelating agent, the

kinetics of enolization, and the kinetics of hydrolysis of corresponding esters. Variations in the pKa and enol content were explained on the basis of steric effects.

A procedure for the separation of lithium from other alkali metal ions was developed, making use of the selectivity of dipivaloylmethane. The theoretical implications of this selectivity are discussed. Correlation of formation constants with a double basicity scale are reviewed. It is suggested that when using such correlations a chelate effect be taken into account. The application of the Edwards and Hammett equation to formation constants is discussed.

Spectrochemistry

1. Development of Spectroscopic Analytical Methods (V. A. Fassel)

1.1 Determination of Small Amounts of Tantalum in Various Materials

When tantalum is used as a container material in experimental reactor loops or in casting rare earth metals, some corrosion of the tantalum results in contamination of the molten metal. The degree of tantalum contamination is determined by fusing the metal sample in a mixture of 2:1 NaOH-Na₂O₂ in nickel crucibles. A selected weight of tantalum-free Nb₂O₅ carrier is added to the fusion mixture prior to the fusion. The ratio of sample to carrier weight is varied depending on the expected tantalum content. For maximum sensitivity, 4 grams of sample and 20 mg. of carrier are used. The fused sample is disintegrated with water containing NH₄Cl. The resulting slurry is acidified with HNO₃ and digested to coagulate the precipitate of Nb₂O₅ which contains the tantalum in the original sample as coprecipitated Ta₂O₅. After filtration, the precipitate is washed with a dilute HNO₃-NH₄NO₃ solution and then dissolved in 1:1 HF. The spectrum of the solution is excited by the rotating disk technique using overdamped condenser discharge excitation. The intensity ratio of the line pair Ta 2685.1 Å/Nb 2664.2 Å is correlated with the tantalum concentration in the usual manner, and referred by calculation to the tantalum content of the original sample.

1.2 Analysis of Binary Alloys of Ta-Zr

A spectrographic method covering the concentration range from 0.1 to 90% Ta has been devised for the binary alloys of Ta-Zr. The samples are dissolved in concentrated HF, and the

solution evaporated almost to dryness. The nearly dry residue is then dissolved and diluted with 1:10 HF and the resulting solution is excited directly by using the rotating graphite disk technique. Unidirectional, overdamped condenser discharges from the multisource are employed for excitation. The polarity of the rotating disk is positive. The intensity ratios of the following line pairs were correlated with concentration in the usual manner, as shown in Table 6.

Table 6

Concentration Range	Line Pair
0.1-2	<u>Ta 2685.11</u> Zr 2713.2
2-50	<u>Ta 2661.336</u> Zr 2670.960
20-65	<u>Ta 2672.497</u> Zr 2670.960
35-85	<u>Ta 2672.497</u> Zr 2667.799
50-90	<u>Ta 2659.41</u> Zr 2667.799

When samples are exposed in triplicate and data from the series of concentration-overlapping line pairs are averaged, analytical results accurate to within 1% can be obtained.

1.3 Separation and Determination of Trace Amounts of Rare Earths in Thorium

A procedure for determination of rare earths in thorium, based on ion-exchange technique, has been under study and preliminary results have been encouraging. The method is based on the fact that thorium forms a soluble neutral $\text{Th}(\text{SO}_4)_2$ complex, whereas the complex rare earth sulfates are monovalent cations. The column, in the anionic cycle, is charged with a dilute HCl solution (pH = 2) of the sample. Subsequent elution with 0.75 M $(\text{NH}_4)_2\text{SO}_4$ removes the thorium by formation of its neutrally charged complex. With

5 gram samples of Th, 99.5% separation has been achieved. Experiments to determine optimum conditions will be continued.

1.4 Determination of Zirconium in Hafnium

A paper entitled "Emission Spectrometric Determination of Low Percentages of Zirconium in Hafnium" by L. S. Gray, Jr., and V. A. Fassel was submitted to Anal. Chem. for publication.

Abstract

The unique similarity in the chemical properties of zirconium and hafnium precludes the use of classical chemical methods for the determination of small amounts of zirconium in hafnium. In this paper emission spectrometric procedures are described for the determination of zirconium in hafnium in the ranges 0.001 to 0.2% using conventional d.c. carbon arc excitation and 0.01 to 0.5% using the conducting briquet excitation technique.

2. Spectroscopic Research (V. A. Fassel)

2.1 Spectrographic Determination of Oxygen in Metals

An investigation of the basic problems involved in determination of oxygen in metals has resulted in the development of a spectrographic technique for this determination. The method has been applied thus far to steels and rare earth metals. For the determination of oxygen in steel, the metal sample is placed in a cavity of a specially designed carbon electrode which forms the anode of a d.c. carbon arc. The arc discharge is operated in a static atmosphere of oxygen-free argon at pressures of approximately 760 mm. When the arc is operated at 20 amperes, the anode cup attains a temperature of about 1700°C. At this temperature the molten metal in the cavity dissolves the carbon retaining wall and forms a molten globule of metal saturated with carbon. The arc strikes directly to this molten globule. The dissolved carbon comes in intimate contact with the combined oxides in the metal, causing their reduction to CO. The evolved CO is dissociated as it passes through the arc and the atomic emission spectrum is excited. Rate studies show that all of the CO is liberated in about 30 seconds.

In rare gas atmospheres it is possible to excite the oxygen triplet at 7771 so that oxygen concentrations in metals as low as a few parts per million can be detected. The oxygen line intensities are very sensitive to the amount of iron volatilized during the excitation process. This can be attributed to the

fact that iron possesses a multitude of excited states as well as an ionization potential well below the 10.7 e.v. required for exciting the oxygen triplet at 7771. In order to compensate for these intensity changes, the intensity ratio of O 7771/A 7891 is measured. The excitation potential of the argon internal standard line is 13.5 electron volts. Because of the similarity in excitation potentials, the intensity of the argon line changes in consort with the oxygen line intensity. The influence of varying amounts of iron volatilized is therefore compensated by internal standardization. The analytical curve for the determination of oxygen in low-alloy steels covers the concentration range 0.002 to 0.1%. The average deviation of the analytical data was + 4% at the higher concentrations and about + 10% at the lower concentrations. The greater deviation at lower concentrations is caused by variations in the oxygen blank.

The extension of this method to other metals of more direct interest to the atomic energy program requires the preparation of standards of known oxygen content. An apparatus for preparing standards by reacting known amounts of molecular oxygen with known weights of metal has been employed for preparing oxygen in lanthanum metal standards.

The simple technique used successfully for determining oxygen in steels failed when applied to lanthanum metal. It has not been established whether the carbon solubility in the lanthanum is too low or whether the dissolution of carbon metal is so slow that an adequate excess of this element is not available in the short time period. The temperature of the electrode cavity may also not be high enough for a rapid reaction. Satisfactory evolution of the CO could be obtained by providing a nickel bath and raising the electrode temperature to 1900°C. The nickel bath is produced by simply fitting a machined nickel cup into the carbon electrode cavity. The sample itself is then fitted into the nickel cup and arced in the usual manner. The reduction reaction now takes place in a ternary liquid bath consisting of nickel, lanthanum, and carbon. The molten alloy dissolves the carbon retaining wall so that the arc strikes directly to the molten globule. An arcing current of 30 amperes is used. Other procedural details parallel those used for the determination of oxygen in steel.

The determination of oxygen in zirconium and titanium has been under investigation, but conditions for quantitative evolution of the CO have not been found. The high thermodynamic stability of the oxides and the high melting points of the carbides are the main obstacles. In principle, much

higher electrode temperatures than those employed thus far can be obtained in a d.c. arc and experimental work using more drastic conditions is now in progress.

2.2 Infrared and Molecular Spectroscopy

A paper entitled "Correlation of Bond Lengths with Stretching Frequency for Carbon-Oxygen and Carbon-Nitrogen Bond Systems" by E. M. Layton, R. D. Kross, and V. A. Fassel was submitted for publication in J. Chem. Phys.

Abstract

Graphical correlations of stretching frequencies with bond lengths for C-O and C-N bond systems in various compounds are presented. For compounds in which stretching frequencies are not subject to vibrational coupling, the average deviations of the points from the respective curves are 0.023 and 0.020 Å.

A report entitled "Infrared Dichroism Studies of Some Molecular Complexes" by R. D. Kross, K. Nakamota, and V. A. Fassel was distributed as ISC-622.

Abstract

The results of a study on the polarized infrared spectra of the hexamethylbenzene-picryl chloride, anthracene-sym-trinitrobenzene, and p,p'-dinitrodiphenyl-p-hydroxydiphenyl molecular compounds show agreement with published x-ray crystal structures. On the basis of the observed dichroism, molecular orientations are suggested for the complexes of picric acid with β -methyl-naphthalene and piperidine.

A report entitled "Infrared Study of Picric Acid Molecular Complexes" by R. D. Kross and V. A. Fassel was distributed as ISC-621.

Abstract

The infrared spectra of 42 picric acid molecular complexes show that the nitro asymmetric stretching and the out-of-plane C-H bending vibrations of the picric acid component are sensitive to complex formation. The frequencies of these vibrations can be correlated with

the type of complex formed, i.e. π - π or n- π type charge transfer. Many of the π - π complexes were found to contain localized intermolecular interactions which give rise to an additional asymmetric stretching vibration. The frequency of the C-H out-of-plane bending vibration of complexed picric acid is an indication of the type of complex formed.

A paper entitled "The Infrared Spectra of Aromatic Compounds. II. Evidence Concerning the Interaction of π -Electrons and σ -Bond Orbitals in C-H Out-Of-Plane Bending Vibrations" by R. D. Kross, V. A. Fassel and M. Margoshes was submitted for publication in J. Am. Chem. Soc., and was distributed as ISC-625.

Abstract

In certain mono- and para-disubstituted benzenes the frequency of one of the C-H out-of-plane bending vibrations falls outside of the characteristic frequency range usually assigned to that vibration. The phenomenon is ascribed to bond rehybridization accompanying the out-of-plane vibrations, whereby the C-H σ -bonds of the benzene nucleus overlap with the π -electrons of the molecules and tend to form sp^3 hybrids. The rehybridization results in decreased effective force constants for the vibrations. The extent of rehybridization depends on the concentration of the π -electrons around the benzene ring, which in turn is dependent on the nature of the substituent. Nitro and carboxyl groups deplete the ring of π -electronic charge so that the σ -bonds undergo a smaller rehybridization. This leads to greater effective force constants, and higher frequencies for the C-H out-of-plane vibrations as compared with compounds in which the substituent is relatively inert with respect to the ring. Bond rehybridization also provides an explanation for the smaller relative intensities of the C-H out-of-plane bending vibrations of compounds such as nitrobenzene as compared with the vibrations of compounds falling in the normal frequency range. Other anomalous spectra are adequately explained on the same basis.

A paper entitled "The Infrared Spectra of Aromatic Compounds. III. The 1045-1185 cm^{-1} Vibration in Monosubstituted Benzenes" by R. D. Kross and V. A. Fassel was submitted for publication in J. Am. Chem. Soc., and was distributed as ISC-620.

Abstract

In monosubstituted benzenes of the type (phenyl) $_n$ M, where

n is the valence of the substituent element M, the frequency of the 1045-1185 cm^{-1} vibration is directly related to the partial ionic character of the $\text{C}_{\text{ar}}\text{-M}$ bond. Using the square of the electronegativity of the substituent as a measure of the bond polarity, a plot is presented which relates this parameter to the corresponding frequency. From the four straight-line curves obtained for group IVB, VB, VIB and VIIB elements, an expression is derived equating electronegativity with the observed frequency. Electronegativity values calculated from this equation compare favorably with accepted values.

3. Spectroscopic Service Analyses (V. A. Fassel)

During the period covered by this report, 3857 samples were analyzed or examined by emission, fluorescence and infrared spectroscopic techniques.

Radiochemistry

1. Tellurium and Antimony Activities (A. F. Voigt)

A report (ISC-665) entitled "The Molecular Chemistry of Antimony and Tellurium" by M. C. Day and A. F. Voigt was distributed.

Abstract

The techniques of scintillation spectrometry have been applied to the study of the radiations of two antimony and two tellurium isotopes. The Iowa State College 70 Mev. synchrotron was used as an x-ray source to produce antimony 127 and antimony 129 by means of a (γ, p) reaction on natural tellurium, and the ground state activities of tellurium 127 and tellurium 129 by means of a (γ, n) reaction on natural tellurium. The energies of both the beta-rays and the gamma-rays have been measured, and where possible, coincidence studies have been made to determine the decay schemes of the isotopes. For the completed decay schemes, spin and parity assignments have been made, and these have been compared with the predictions of the shell model of the nucleus.

A method of isotopic enrichment was developed for the preparation of the tellurium beta-ray sources. This is based upon a change in chemical valence as the result of the recoil of a (γ, n) reaction on the tellurium nucleus. For the preparation of both the tellurium sources and the

antimony sources, the activities under study were purified by a second precipitation with hold-back carriers to prevent any serious contamination by other activities that might be present. In all cases the half life was followed as a check of the isotopic purity.

The 9.3 hour isomer of tellurium 127 was found to decay by a simple beta-ray with an end-point energy of 0.683 ± 0.010 Mev. The log ft value was calculated to be 5.6. This indicates that the transition is of the allowed type and a spin change of $\Delta I = 0, \pm 1$ and no change in parity would be expected. This is consistent with the proposed level assignments of $d_{3/2}$ for the tellurium 127 and $d_{5/2}$ for the iodine 127 ground states. The 72 minute isomer of tellurium 129 was found to decay by means of two beta-rays of 1.46 ± 0.01 and 1.01 ± 0.02 Mev. and two gamma-rays of 0.450 ± 0.005 and 0.035 Mev. Coincidence studies showed that the two gamma-rays are in coincidence, the 1.46 Mev. beta-ray is in coincidence with the 0.035 Mev. gamma-ray, and the 1.01 Mev. beta-ray is in coincidence with the 0.450 Mev. gamma-ray. The log ft values were calculated to be 5.8 for both of the beta-ray transitions which indicates that both of the transitions are allowed. A disintegration scheme and level assignments were proposed in which approximately 80 percent of the transitions from the initial $d_{3/2}$ state occur through the 1.46 Mev. beta-ray to a level of spin either $3/2$ or $5/2$. The remaining 20 percent go through the 1.01 Mev. beta-ray to a level of spin $1/2$ followed by the 0.450 Mev. gamma-ray to the same $3/2$ or $5/2$ level. The 0.035 Mev. transition occurs in both cases to the $g_{7/2}$ ground state of iodine 129.

The decay of the antimony 127 was found to be very complex. Three beta-ray groups were determined with end-point energies of 1.57 ± 0.03 , 1.11 ± 0.03 , 0.857 ± 0.021 Mev., and eight gamma-rays were observed with energies of 0.056 , 0.185 , 0.240 ± 0.003 , 0.456 ± 0.004 , 0.417 , 0.563 ± 0.005 , 0.674 ± 0.005 , and 0.764 Mev. By means of coincidence measurements, it was found that the 0.674 Mev. gamma-ray is in coincidence with the 0.857 Mev. beta-ray, and the 0.240 and the 0.456 Mev. gamma-rays are in coincidence with the 1.11 Mev. beta-ray. Four gamma-rays with energies of 0.165 ± 0.005 , 0.308 ± 0.004 , 0.534 ± 0.003 , and 0.788 ± 0.005 Mev. were observed in the decay of the 4.2 hour antimony 129 activity. The end-point energy of the highest energy beta-ray group was found to be 1.87 ± 0.05 Mev. Coincidence studies indicated a beta-ray group of 1.21 Mev. in coincidence with the

0.788 Mev. gamma-ray and a beta-ray of 1.47 Mev. in coincidence with the 0.534 Mev. gamma-ray. However, the intensities of the antimony 129 activities were too low to give statistically significant data for satisfactory coincidence studies.

2. Extraction of Thallic Chloride into Ether (A. F. Voigt)

A report (ISC-703) entitled "The Formation of Thallium Chloride Complexes and Their Extraction into Ether" by D. L. Horrocks and A. F. Voigt is being distributed.

Abstract

Thallium is one of a large group of elements which can be extracted into ethers from halogen acid solutions. The general lack of knowledge of the extraction process for these salts has given strong impetus to the study of all aspects of it.

Since there has been no previous investigations on the fundamental nature of the extraction of thallium-chloride complexes from HCl solutions, it was the purpose of this work to study the extraction under various conditions, using radio tracer techniques as the tool. This investigation, employing isopropyl ether, had as its immediate objective the determination of the empirical formula of the thallium compound in the ether phase and the equilibrium constant for the extraction process.

In this investigation it was found necessary to study the extraction at constant, but high, ionic strength. Since the extraction equilibrium constant is a function of the activities of the thallium-chloride complexes, the activity coefficients and the concentrations of the various complexes need to be known, and the usual methods of determining the activity coefficients, such as simple extensions of the Debye-Huckel law, could not be used at these high values of the ionic strength. Methods and equations were developed to determine ~~these~~ activity coefficients. This method is applicable to systems in which the ionic strength is constant, the complex ions are large and the concentrations of the complexes are small.

It was found that the compound present in the ether phase was essentially HTlCl_4 , and the equilibrium constant for the extraction was defined as:

$$K = \frac{(\text{HTlCl}_4)_e}{(\text{H}^+) (\text{TlCl}_4^-)}$$

where the parentheses indicate activities and the subscript "e" indicates the ether phase. For investigations performed at constant acidity a new extraction equilibrium constant was defined:

$$K' = K(\text{H}^+) = \frac{(\text{HTlCl}_4)_e}{(\text{TlCl}_4^-)} \quad .$$

The investigation revealed that for a given constant acid concentration K' was essentially constant with varying LiCl concentrations for LiCl concentrations greater than 0.1 M. At LiCl concentrations below 0.1 M. K' increased quite markedly. This increase was believed due to the extraction of TlCl_3 and/or the ionization of HTlCl_4 in the ether phase at low etheral concentrations of thallium. The extraction was dependent upon the ionic strength as shown by the change in K' , at a given acidity, with change in the value of the ionic strength. For 1.0 M. HClO_4 the value of K' was 2.50 at the value of ionic strength equal to 2.0 and 5.35 at an ionic strength value equal to 3.0.

It was observed that K' was dependent upon the concentration of HClO_4 to the first power. Also the overall distribution coefficient of thallium between the aqueous and ether phases, K_T , was observed to be dependent upon the first power of the HClO_4 concentration.

The true extraction equilibrium constant was:

$$K_x = \frac{(\text{HTlCl}_4)_e}{(\text{HTlCl}_4)_w} \quad .$$

Although K_x could not be directly calculated, quantities

which were proportional to K_x were calculated. At HClO_4 concentrations greater than 0.4 M. and LiCl concentrations greater than 0.1 M. the species extracted into isopropyl ether was shown to be HTlCl_4 . At very low LiCl concentrations, below 0.05 M., the extraction was a more complicated process.

The extraction data indicated the formation of a pentachlorothallium complex. The formation constant for the complex, TlCl_5^{-2} , from thallium (III) and chloride ions was calculated to be 3.6×10^{17} .

3. Szilard-Chalmers Processes (D. S. Martin)

A paper, "Szilard-Chalmers Process for Osmium from Hexachloroosmate(IV) Targets", by R. F. Mitchell and D. S. Martin, Jr., was submitted for publication in J. Inorg. Nucl. Chem.

Abstract

The experimental conditions are described for a Szilard-Chalmers separation of $\text{Os}^{191\text{m}}$ formed by (γ, n) reactions on $(\text{NH}_4)_2 \text{OsCl}_6$ targets. The activity was carried preferentially with the initial fraction of OsO_4 which was distilled from boiling HNO_3 solutions of the target compound. Enrichment factors of 10 were obtained for 60 percent of the activity. However, the $\text{Os}^{191\text{m}}$ was not carried by OsO_4 carrier which was extracted into CCl_4 from the initial target compound solutions. The separation, therefore, was accomplished by the rapid HNO_3 oxidation of reactive intermediate species. Apparently ammonium ion was beneficial, for the potassium salt gave markedly inferior concentrations.

In another Szilard-Chalmers process the fate of $\text{Co}^{58\text{m}}$ (9 hrs.) prepared by the (γ, n) process on targets of $[\text{Co}(\text{en})_3](\text{NO}_3)_3$ crystals was followed. (en = ethylenediamine). It was found that if the crystals were dissolved immediately after a 4-hr. irradiation ca. 52% of the activity followed Co^{++} in a precipitation of its hydroxide. (Form I). Successive recrystallization of the tris(ethylenediamine)cobalt(III) nitrate gave decreasing specific activities in the crystals. However, when the bromide was recrystallized four times, lower specific activities were obtained which were not reduced by further recrystallizations. The Co^{58} content which corresponded to the upper limit of retained activity in the complex was 22% (Form II). An additional fraction (Form III) was about 26%. Its chemical identity was not determined but it was presumably a $\text{Co}(\text{III})$ complex. There were no appreciable changes in these fractions (if the crystals were stored at room temperature

for the 2-4 day duration) which could be studied with the activity available. It is of interest that the distribution of activities among these fractions is somewhat different than found by Zuber and Miller (thesis by Zuber submitted to Columbia University) for (n, γ) activations. Changes in the fractions were noted in the aging of the crystals at high temperatures. Thus, the crystals appeared to heal the imperfections which contained the activated Co and significant amounts of the activity were reincorporated into the actual target complex in the process. The healing process was observed to continue for about 20-25 hrs. at 108°C . During this period the distribution of activity between the fractions underwent a change. The changes observed in the fractions during aging were:

(1) 52% \longrightarrow 26%; (II) 22% \longrightarrow 65%; (III) 26% \longrightarrow 9%.

4. Exchange Reactions (D. S. Martin)

Isotopic exchange studies with Cl^{36} have yielded important information about the behavior of the aqueous systems containing PtCl_4 , $\text{PtCl}_3(\text{H}_2\text{O})$ and Cl^- [L. F. Grantham, T. S. Elleman and D. S. Martin, J. Am. Chem. Soc., 77, 2965 (1955)]. The experiments are now being extended to solutions prepared from the complex salt $\text{K}[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]$ and chloride. It has been found that the ion $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^-$ undergoes an aquation which is very similar to the one for PtCl_4 . Since the solutions become acidic, the H_2O must replace a Cl^- rather than the NH_3 . The reaction is therefore $[\text{PtCl}_3(\text{NH}_3)]^- + \text{H}_2\text{O} \longrightarrow \text{PtCl}_2(\text{NH}_3)(\text{H}_2\text{O}) + \text{Cl}^-$. The aquo-ion is weak acid with a pH of about 7. A tentative value for the first order aquation rate constant is $1.83 \times 10^{-5} \text{ sec}^{-1}$ and the equilibrium constant is 0.0114 at 20°C . Addition of tetraphenyl arsonium ion precipitates only the trichloroamineplatinate(II) ion, whereas the neutral complex and the chloride remain in solution. Exchange has been followed under a variety of conditions. The aquation process does not account for the total exchange rate. Under conditions in which only small amounts of the aquo-species exist an additional exchange rate approximately equal to the aquation rate occurs which is first order in the complex and independent of chloride. Even when the aquo-complex amounts to half the total platinum, no additional exchange process was noticed. There is then the similarity with the (PtCl_4) system that only a (-1) ion undergoes a measurable first order exchange, independent of chloride. It is noteworthy that both the cis- and trans-chlorides are exchanged at comparable rates. However, the data cannot distinguish between the case in which one type of chloride was replaced by only the aquation mechanism with the other by direct exchange only, and the case in which all three chlorides are equivalently susceptible to aquation and exchange. The results

appear to imply that the direct exchange must occur by an SN 1 mechanism and the aquation must require a fundamentally different transition state in an SN 2 process.

5. Solubility Determinations (D. S. Martin)

A report (ISC-660) entitled "Iodato-Silver Complexing Equilibria" by J. J. Renier and D. S. Martin, Jr., was distributed.

Abstract

Solubilities of silver iodate in aqueous solutions containing various concentrations of lithium iodate have been measured for 25.0°C., 35.0°C. and 50.0°C. by means of an improved radioassay technique for silver activity. They have also been measured for the same temperatures in aqueous solutions containing various proportions of lithium iodate and lithium perchlorate. In the latter experiments, the ionic strengths of all equilibrium solutions were fixed at a value of 1.00 M.

The refined radiotracer method was based upon an electrodeposition procedure for mounting samples for counting. Samples of the equilibrium solution phases from the equilibrated mixtures were carefully added to portions of strong nitric acid solutions which contained a pre-determined amount of silver carrier (usually 10 mg.). To insure complete exchange between the tracers and the carriers, the solutions were evaporated to dryness. The residues were subsequently dissolved in ammoniacal cyanide plating baths and a current of 0.2 amp was passed through the resulting solutions for a period of thirty-five minutes. The silver that was uniformly deposited was determined gravimetrically and was counted to determine its activity. From these data the activities corresponding to 100 percent recovery of the carriers were computed. The applications of corrections for self-absorption and radioactive decay converted the observed activities to ones which were proportional to the tracer concentrations in the various aliquots of the equilibrium solution phases. A knowledge of the specific activity of the silver used in the experiments made the radioassay complete.

A series of experiments performed to test the procedure for sampling of equilibrated mixtures have been discussed at some length. The results have indicated that an evaluation of the method used to obtain equilibrium solution samples should form an integral part of all solubility measurements in which radiotracers are employed.

The solubility data have been interpreted in terms of chemical equilibria which involve the species Ag^+ , AgIO_3 (aq.), and $\text{Ag}(\text{IO}_3)_2^-$. Equilibrium solubility product constants for AgIO_3 (s) in aqueous solution were obtained from the results of measurements performed in solutions for which ionic strengths were low and variable. The values of these quantities for 25.0°C., 35.0°C. and 50.0°C. were observed to be $(3.0 \pm 0.15) \times 10^{-8}$, $(6.3 \pm 0.3) \times 10^{-8}$ and $(17.4 \pm 1.0) \times 10^{-7}$ respectively. Equilibrium formation constants for the monoiodatosilver and the diiodatosilver complexes were estimated from the measurements performed for solutions of constant ionic strength. At 25.0°C., 35.0°C. and 50.0°C. the values determined for the monoiodatosilver species were 4.26 ± 2.62 , 6.34 ± 1.86 and 9.09 ± 1.16 respectively, while those for the diiodatosilver species were 79.4 ± 5.2 , 66.4 ± 4.3 and 41.1 ± 3.0 respectively. It was observed that representations of the experimental data obtained for low, variable ionic strengths were adequately reproduced by means of suitable equations and the equilibrium formation constants obtained for constant ionic strength.

From the solubilities and their temperature coefficients, thermodynamic quantities for the iodate complexes have also been computed. The entropy change calculated for the reaction to form AgIO_3 (aq.) was 20.3 ± 14.7 e.u. and that calculated for the reaction to form $\text{Ag}(\text{IO}_3)_2^-$ was -8.50 ± 2.55 e.u. These values were found to be in fair agreement with a semi-empirical formulation.

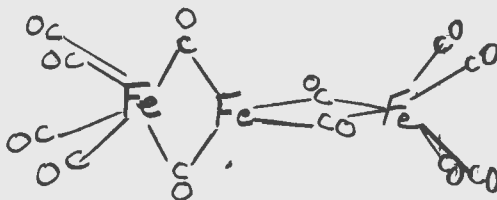
The thermodynamic description of the silver iodate-iodate ion-water system that was obtained was not definitive in an absolute sense, in that iodate ion appeared to be a very weak complexing agent for silver, and the monoiodatosilver species possessed a low stability which was difficult to evaluate quantitatively.

X-Ray Chemistry

1. Structure of Iron Tetracarbonyl- $\text{Fe}(\text{CO})_4$ (R. E. Rundle)

Iron tetracarbonyl is a tetramer at ordinary temperatures, and its structure is a complex problem, since usual valence bond structure would lead to a paramagnetic compound, whereas the carbonyl has been shown to be diamagnetic.

The most nearly accepted structure, due to Sheline, [R. K. Sheline, J. Am. Chem. Soc., 73, 615 (1951)] is:



where the configuration about the central iron is tetragonal.

We have examined the crystal structure of the carbonyl, finding it monoclinic, $P2_1/n$, with $a=8.87$, $b=11.34$, $c=8.34\text{\AA}$, $\beta=97^\circ 9\frac{1}{2}'$. There are two molecules per unit cell, which should then have a center of symmetry, and the iron atoms should be easily located, which did not turn out to be the case.

The structure analysis has proceeded through a complete three-dimensional Patterson, analysis of which seems to indicate that the structure has a disorder, but that the molecule has an essentially equilateral triangle of iron atoms, and the molecules each have two equally probable orientations which differ by rotation about the molecular 3-fold axis by 60° .

2. X-Ray Investigation of "Tin Whiskers" (R. E. Rundle)

2.1 Introduction

A number of articles have been published recently on "whiskers" of tin, as well as of some other metals. It has been reported that their mechanical properties are markedly different from bulk specimens and these properties have been attributed to the possibility that the whiskers are perfect or near-perfect crystals, essentially free of dislocations.

The investigation of tin whiskers in this laboratory developed from research on some Zr-Sn alloys. Several months after preparation of two tin-rich alloys, whiskers were observed growing out of the surface of some unreacted tin. The unreacted tin contained a small amount of an unknown phase.

We thought it would be of interest to determine whether the whiskers were perfect or mosaic by x-ray diffraction methods, since the diffraction intensities of a perfect crystal differ from a mosaic crystal if the crystals are larger than a critical size. (ca. 1 micron).

2.2 Experimental

The whiskers consist of three types: straight, kinked and shriveled. We shall only discuss the first type here. Their diameters range from about 1-15 microns and their lengths are a few tenths of a millimeter, although some are longer than a millimeter.

X-ray diffraction photographs were taken of about a dozen whiskers. They have been observed growing along the $\langle 001 \rangle$, $\langle 100 \rangle$, $\langle 101 \rangle$, and $\langle 111 \rangle$ directions.

Intensity data were taken of four crystals. Data for I and II were taken on a Weissenberg camera with Mo radiation using multiple film and timed exposures. The intensities were estimated visually and corrected for the Lorentz-polarization factor. Intensity data for III and IV were taken with a Geiger counter attachment on a Weissenberg camera using Cu K α radiation and also corrected for the L_p factor.

The diameters of the crystals are 10μ , 2μ , 5.5μ and 11 ($\pm 0.5\mu$) for I, II, III, and IV, respectively. The corresponding absorption factors, μ_r , are 0.1, 0.02, 0.51 and 1.1 (assuming the whiskers to be cylindrical). From International Tabellen, Vol. II, it is seen that absorption is negligible for data taken with Mo radiation (I and II), but is not negligible for data taken with Cu radiation (III and IV). Although the absorption does not vary greatly with increasing Bragg angle, θ , the absorption corrections for equivalent reflections are different due to the small deviations in cross section from a true cylinder. A 10% difference in diameter can affect the intensity by 10-15% at the same Bragg angle. Consequently, intensity data for crystals III and IV were averaged for all equivalent reflections.

2.3 Discussion

On the basis of theory, it is concluded that the whiskers studied are not perfect crystals, although they do seem to have a higher degree of perfection than is usually attributed to bulk specimens in general (usually assumed less than 10^{-4} cm). It should be mentioned that in this investigation only the cross section of the crystallites normal to the whisker axis was measured; however, it does not seem likely that the dimension of the crystallites along the whisker axis would be much different from that obtained for the other directions.

The whiskers used by Herring and Galt \langle C. Herring, J. K. Galt, Phys. Rev., 85, 1060 (1952) \rangle in their initial observations

of the remarkable mechanical properties of tin whiskers were 1.3 ~~in~~ in diameter. Whiskers of this size may be perfect in cross section, but it seems reasonable that they too would exhibit imperfections along the whisker axis.

Although no experiments on their mechanical properties were performed here, the whiskers appeared to possess the unusual elastic properties described by Herring and Galt. For example, they could be bent into approximately a closed circle and when released, would immediately return to their original shape. According to Eshelby, [J. D. Eshelby, J. Appl. Phys., 24, 176 (1953)] it is not necessary to postulate the absence of imperfections in order to account for these observations.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-575 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. October, November, December, 1954.
- ISC-604 F. H. Spedding, J. E. Powell and E. J. Wheelwright. The Stability of the Rare Earth Complexes with N-Hydroxyethylethylenediaminetriacetic Acid.
- ISC-605 Ames Laboratory Staff. Engineering. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-606 Ames Laboratory Staff. Chemistry. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-607 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-608 Ames Laboratory Staff. Physics. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-609 Compiled by P. Chiotti and O. N. Carlson. Hanford Slug Program. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-611 F. H. Spedding and J. E. Powell. A Laboratory Method for Separating Nitrogen Isotopes by Ion-Exchange.
- ISC-612 A. W. Andresen and G. L. Bridger. Recovery of Uranium from Superphosphates.
- ISC-617 J. E. Powell and F. H. Spedding. Basic Principles Involved in the Macroseparation of Adjacent Rare Earths from Each Other by Means of Ion-Exchange.
- ISC-620 R. D. Kross and V. A. Fassel. The Infrared Spectra of Aromatic Compounds. III. The 1045-1185 cm^{-1} Vibration in Monosubstituted Benzenes.
- ISC-621 R. D. Kross and V. A. Fassel. An Infrared Study of Picric Acid Molecular Complexes.

- ISC-623 L. S. Gray and V. A. Fassel. Emission Spectrometric Determination of Low Percentages of Zirconium in Hafnium.
- ISC-625 R. D. Kross, V. A. Fassel and M. Margoshes. The Infrared Spectra of Aromatic Compounds. II. Evidence Concerning the Interaction of π -Electrons and σ -Bond Orbitals in C-H Out-of-Plane Bending Vibrations.
- ISC-629 R. T. Nichols and E. N. Jensen. The Decay Scheme of Sc^{147} .
- ISC-630 P. Hall and S. Legvold. Remanent Magnetism in Toroids.
- ISC-632 J. T. Jones, Jr., and J. K. Knipp. Notes on Hyperfragments.
- ISC-633 E. M. Layton, Jr., R. D. Kross and V. A. Fassel. A Correlation of Bond Length with Stretching Frequency for C-O and C-N Systems.
- ISC-634 G. H. Beyer, E. L. Koerner and E. H. Olson. Conversion of Zirconium Sulfates to Anhydrous Zirconium Tetrafluoride.
- ISC-637 E. Wheelwright and F. H. Spedding. The Use of Chelating Agents in the Separating of the Rare Earth Elements by Ion-Exchange Method.
- ISC-640 P. Chiotti, P. F. Woerner, H. H. Kepfer, K. J. Gill and R. E. Cutrell. Application of Metal Coatings on Uranium-Summary Report.
- ISC-641 Compiled by P. Chiotti and O. N. Carlson. Hanford Slug Program. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-642 Ames Laboratory Staff. Engineering. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-643 Ames Laboratory Staff. Chemistry. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-645 Ames Laboratory Staff. Physics. Quarterly Summary Research Report. April, May, June, 1955.

- ISC-656 P. Chiotti, H. H. Klepfer and K. J. Gill. Uranium-Zinc System.
- ISC-661 J. S. Fritz and S. A. Sutton. Titration of Mercury with Bis(2-Hydroxyethyl) Dithiocarbamate.
- ISC-665 M. C. Day and A. F. Voigt. The Molecular Chemistry of Antimony and Tellurium.

2. Papers Published in Scientific Journals

- Corbett, J. D. and R. K. McMullan
The Lower Oxidation States of Gallium. I. The $\text{GaI}_3\text{-GaI}$ System. J. Am. Chem. Soc. 77, 4217-19 (August, 1955).
- Corbett, J. D. and S. von Winbush
The Solubility of Some Metals in Their Molten Halides. J. Am. Chem. Soc. 77, 3964-66 (August, 1955).
- Day, M. C., G. W. Eakins and A. F. Voigt
The Disintegration Schemes of the Te^{127} and Te^{129} Ground States. Phys. Rev. 100, 796-8 (November, 1955).
- Freeland, M. Q. and J. S. Fritz
High Precision Micro Spectrophotometric Analysis with Application to V-Al Alloys. Anal. Chem. 27, 1737-41 (November, 1955).
- Fritz, J. S. and M. Johnson
Volumetric Determination of Zirconium. Anal. Chem. 27, 1653-5 (October, 1955).
- Fritz, J. S. and S. S. Yamamura
Rapid Microtitration of Sulfate. Anal. Chem. 27, 1461-64 (September, 1955).
- Hansen, R. S.
The Theory of Vibration Jets in Liquids of Variable Surface Tensions. ISC J. of Sci. 30, 301-11 (November, 1955).
- Happe, J. A. and D. S. Martin, Jr.
Isotope Exchange of Manganese during the Reaction between Manganese(II) and Permanganate. J. Am. Chem. Soc. 77, 4212-17 (August, 1955).
- Herwig, L. O., G. H. Miller and N. G. Utterback
Some Characteristics of a Gridded Parallel-Plate Ionization Chamber. Rev. Sci. Instr. 26, 929-36 (October, 1955).

- Hettel, H. J. and V. A. Fassel
Determination of Fractional Part Per Million Amounts of Certain Rare Earths in Zirconium Metal. Ion Exchange Separation-Spectrographic Determination. Anal. Chem. 27, 1311 (August, 1955).
- Jones, J. T., Jr., and J. K. Knipp
Notes on Hyperfragments, Nuovo Cimeneto 2, 857-9 (October, 1955).
- Kniseley, R. N. and V. A. Fassel
A Rotating Step Sector for Use with AC or Other Intermittent Spectrographic Light Sources. J. Opt. Soc. 45, 1032-4 (December, 1955).
- Kross, R. D. and V. A. Fassel
The Infrared Spectra of Aromatic Compounds. III. The 1045-1185 cm^{-1} Vibration in Monosubstituted Benzenes. J. Am. Chem. Soc. 77, 5858-9 (November, 1955).
- Laslett, L. J. and D. J. Zaffarano
Nuclear Research with High Energy X-Rays at Iowa State College. The Science Counselor (September, 1955).
- Nichols, R. T. and E. N. Jensen
Decay Scheme of Sc^{47} . Phys. Rev. 100, 5, 1407-1409 (December, 1955).
- Ring, L. S., Jr.
The Photodeuteron/Photoproton Yield from Sulfur. Phys. Rev. 99, 137-8 (July, 1955).
- Rundle, R. E.
The Structure of Ice. J. Phys. Chem. 59, 680-81 (August, 1955).
- Simmons, C. R. and R. S. Hansen
Solvolysis of Hafnium and Zirconium Tetrachlorides in Methyl and Ethyl Alcohols. J. Phys. Chem. 59, 1072-3 (October, 1955).
- Skochdopole, R. E., M. Griffel, and F. H. Spedding
The Heat Capacity of Erbium from 15-320°K. J. Chem. Phys. 23, 12, 2258-63 (December, 1955).
- Spedding, F. H. and J. L. Dye
The Vapor Pressure of Mercury at 250-360°C. J. Phys. Chem. 59, 581-3 (July, 1955).
- Spedding, F. H. and J. E. Powell
A Laboratory Method for Separating Nitrogen Isotopes by Ion-Exchange. J. Am. Chem. Soc. 77, 6125-32 (December, 1955).

Stone, J. F., D. Kirkham and A. A. Read
 Soil Moisture Determination by a Portable Neutron-
 Scattering Moisture Meter. Soil Sci. Soc. of Am. Proc.
19, 419-23 (October, 1955).

Wilhelm, H. A. and B. A. Rogers
 The Physical Metallurgy of Thorium. IMD. Spec. Report
 Series #1 (~~American~~ Institute of Mining, Metallurgical and
 Petroleum Engineering) (October, 1955).

APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
National Bureau of Standards Washington, D. C.	1 lb. lanthanum metal 1 lb. cerium metal 1 lb. neodymium metal 1 lb. praseodymium metal 10 gm cerium metal
Argonne National Laboratory Lemont, Illinois	1 sample each of: neodymium metal samarium metal
Dr. J. R. Gump Michigan Chemical Corporation St. Louis, Michigan	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Battelle Memorial Institute Columbus, Ohio	1 gm thulium metal, tantalum-free
New Brunswick Laboratory New Brunswick, New Jersey	2 gm dysprosium oxide 2 gm erbium oxide 2 gm samarium oxide 20 gm yttrium oxide 100 mg lutetium oxide 1 gm ytterbium oxide
Research Laboratories of Colorado, Inc. Newtown, Ohio	3 thulium pellets

State University of Iowa
Department of Physics
Iowa City, Iowa

5 gm N^{14} isotope

University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

2 gm pure terbium oxide
10 gm neodymium metal
20 gm erbium metal
20 gm yttrium metal
66 gm neodymium metal
69 gm samarium metal
72 gm gadolinium metal
77 gm erbium metal

Transportation Officer
Fort Totten, New York

6 thulium buttons

University of Minnesota

1 gm lanthanum metal
1 gm cerium metal
1 gm praseodymium metal
1 gm neodymium metal
1 gm samarium metal
1 gm gadolinium metal
1 gm erbium metal
1 gm yttrium metal
1 gm dysprosium metal
1 gm ytterbium metal

Professor C. D. Jefferies
University of California
Berkeley, California

200 mg high purity lanthanum
oxide
2 gm lanthanum oxide
10 mg terbium oxide

Knolls Atomic Power Laboratory
Schenectady, New York

100 mg neodymium oxide
100 mg lanthanum oxide
200 mg erbium oxide
100 mg samarium oxide
100 mg praseodymium oxide
200 mg holmium oxide
200 mg lutetium oxide
200 mg ytterbium oxide
200 mg thulium oxide
200 mg dysprosium oxide
200 mg terbium oxide
100 mg gadolinium oxide
100 mg cerium oxide
100 mg yttrium oxide
1 gm lanthanum oxide
1 gm cerium oxide
1 gm praseodymium oxide
1 gm neodymium oxide
1 gm samarium oxide
1 gm gadolinium oxide
1 gm yttrium oxide

American Metallurgical Products Co.
New Castle, Pennsylvania

$\frac{1}{4}$ lb. praseodymium metal
 $\frac{1}{4}$ lb. neodymium metal

Brookhaven National Laboratory
Upton, Long Island, New York

5 gm pure thulium oxide
10 gm yttrium oxide
25 gm lanthanum metal
25 gm praseodymium metal
25 gm samarium metal
100 gm cerium metal

Dr. R. B. Price
Battelle Memorial Institute
Columbus, Ohio

2 gm thulium metal

Army Medical Research Laboratory
Fort Knox, Kentucky

8 thulium buttons

C. A. Hutchison
Chicago, Illinois

2 gm praseodymium oxide
1 gm neodymium oxide
1 gm gadolinium oxide
 $\frac{1}{2}$ gm terbium oxide

Mr. H. A. Boorse
Pupin Physics Bldg.
New York, New York

1 cylinder lanthanum metal

Dr. Richard L. Caldwell
Magnolia Petroleum Co.
Dallas, Texas

1 thulium pellet

Dr. J. M. Daniels
Department of Physics
University of British Columbia
Vancouver, B. C., Canada

5 gm ytterbium oxide

Dr. Wm. F. Wagner
Chemistry Department
University of Kentucky
Lexington, Kentucky

1 gm lanthanum oxide
1 gm cerium oxide
1 gm praseodymium oxide
1 gm neodymium oxide
1 gm samarium oxide
1 gm gadolinium oxide
1 gm yttrium oxide
100 mg terbium oxide
100 mg dysprosium oxide
100 mg holmium oxide
100 mg erbium oxide
100 mg ytterbium oxide
100 mg thulium oxide
100 mg lutetium oxide

Johns Hopkins University
Baltimore, Maryland

10 gm terbium oxide